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LXXIV. *The Temperature Variation of Intrinsic Magnetization and Associated Properties of Ferromagnetics.* By EDMUND C. STONER, Ph.D. (Cambridge), Reader in Physics at the University of Leeds*.

Introduction.

FERROMAGNETIC phenomena may be conveniently divided into two groups, those typified by the variation, in strength and direction, of the magnetization at a single temperature, with strength and direction of an applied field, and those typified by the variation of specific heat with temperature. The general characteristics of both groups of phenomena may be at least qualitatively explained by assuming the existence in the ferromagnetic of an intrinsic or spontaneous magnetization which varies with the temperature, and which is approximately equal to the saturation magnetization, as ordinarily measured, at the particular temperature.

In determining the intrinsic magnetization the various secondary effects may be eliminated by using high fields (10-20 kilogauss); the magnetization is observed in different fields and by extrapolation to zero field the intrinsic magnetization may be determined. By carrying out measurements at different temperatures the variation of the intrinsic

* Communicated by Prof. R. Whiddington, D.Sc., F.R.S.

magnetization with temperature may be found. In those properties which depend on the energy associated with the intrinsic magnetization, such as the "magnetic" specific heat, the secondary influences play a negligible role. It is thus possible to determine values for the intrinsic magnetization and for various associated properties, corresponding to the idealized isotropic ferromagnetic, from experiments on the ordinary polycrystalline material. The most accurate data available are those for nickel, which will be considered in most detail.

Intrinsic magnetization occurs in ferromagnetics owing to the special character of the interaction between the "carriers" of the magnetic moment⁽¹⁾. Heisenberg has considered a model in which each atom has one electron in addition to those forming completed configurations, and has shown that the interchange interaction between electrons in neighbouring atoms will give rise to effects which have been formally correlated by the Weiss molecular field hypothesis. The relation between the Heisenberg and Weiss theories has been discussed in a previous paper⁽²⁾. That a ferromagnetic in bulk may be unmagnetized in the absence of an external field is due to the intrinsic magnetization being constant in direction only throughout limited "domains," which may be micro-crystals or merely groups of atoms. The effect of an external field is to render the intrinsic magnetization apparent, by bringing the directions of magnetization in the different domains towards parallelism.

It is the intrinsic magnetization, and effects depending on it, which will be considered in this paper, which follows the line of development which originated in Weiss's modification of Langevin's theory of paramagnetism. The intrinsic magnetization is that which would be characteristic of an idealized isotropic ferromagnetic, free from distortion, in a vanishingly small external field. In a perfect crystal there are complications which may be attributed to a "crystalline field." As the result of the work of, among others, Mahajani, Akulov, Becker, and Powell, considerable progress has been made in showing how this field may arise, and in correlating the experimental results now available for single crystals. There are further effects due to distortions of any kind. The crystalline and distortional effects are of the greatest importance, for without them ordinary polycrystalline ferromagnetic materials would not have many of their most familiar characteristics; but in one sense these are secondary characteristics superposed on those of the idealized isotropic ferromagnetic.

There is now a considerable amount of evidence as to the nature of the carriers in ferromagnetics. The gyromagnetic ratio shows that the carriers are such that the g value (the ratio of the magnetic to the mechanical moment, both measured in Bohr units) is 2^* . This result indicates that, at the temperature at which the gyromagnetic experiments have been carried out, the magnetic moment is due to electron spin; but it is important to notice that it does not, by itself, make it possible to decide whether the spins are those of free or bound electrons. Other evidence, however, makes it practically certain that the spins are not those of free electrons^(2,3). Further, taking the electrons as bound (in some sense), it remains to be decided whether the spins are independent or combined to give a resultant (when the atom or ion in an S state would more properly be regarded as the carrier), and whether the spins are those of electrons in excess of those forming a completed configuration, or of "deficient electrons" (the particular group containing more than half and less than the whole of the number of electrons required for completion).

In connexion with the question of the independence of electron spins, it has been shown by Tyler^(4,5) that the intrinsic magnetization temperature curves for iron and cobalt as well as for nickel agree much more closely with the theoretical curve corresponding to carriers for which $j = \frac{1}{2}$ than with the curves for which j has a value of 1 or more (including the classical curve). There must certainly be more than one "magnetic electron" per atom in iron, and the evidence for the carriers having a j value of $\frac{1}{2}$ and a g value of 2 indicates that, as a first approximation, they may be taken to be independent electron spins. The changes of specific heat at the Curie point lend support to this conclusion⁽²⁾. Evidence as to whether the spins are those of excess or deficient ("missing") electrons is possibly provided by the thermoelectric characteristics of ferromagnetics⁽⁶⁾.

As has been previously discussed⁽²⁾, the formulæ derived in Heisenberg's treatment of ferromagnetism are unsatisfactory as a representation of the behaviour of ferromagnetics, the discrepancies being due to terms which arise owing to special assumptions made as to the energy distribution of states corresponding roughly to a particular value of the

* This value is approximate. S. J. Barnett obtains consistently values less than 2 by about 5 per cent., which he considers outside the limits of experimental error. *Phys. Rev.* xxxvi. p. 789 (1930). This is consistent with the view discussed later.

magnetization. It has been shown by Powell⁽⁷⁾ that these terms become of less importance if the interaction is appreciable between the spins of electrons in atoms which are not closest neighbours. (This has the effect of making larger the effective z , which in Heisenberg's theory corresponds to the number of neighbouring atoms.) Powell brings forward evidence in favour of this view. Justification is thus provided for a very simple treatment of the interaction theory^(2, 8), which certainly gives a much closer representation of the experimental facts.

The above considerations indicate that it is reasonable to take as a first approximation to an actual ferromagnetic an idealized model, in which the magnetization is due to electron spins, these being the "carriers," the quantum interchange interaction between them giving rise to the Weiss molecular field effects. Some of the characteristics of this model have already been considered⁽²⁾. In the next section the properties of the model, assumed, for simplicity, to have one magnetic electron per atom, will be dealt with more completely; the properties will then be compared with those of actual ferromagnetics, and the significance of the similarities and differences will be discussed.

The Idealized Ferromagnetic.

For a ferromagnetic in which there is one effective electron spin moment per atom, the intrinsic magnetization is determined by the equations

$$\sigma/\sigma_0 = \tanh a, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\sigma/\sigma_0 = \frac{MRT}{N\rho\sigma_M^2} a = \frac{T}{\theta} a. \quad . \quad . \quad . \quad . \quad (2)$$

Here σ is the specific intensity magnetization, σ_0 the saturation value; σ_M the saturation moment per gram molecule. Let L be Avogadro's number, μ the magnetic moment per atom (in the present case, $\mu = \mu_B$),

$$\sigma_M = L\mu = M\sigma_0 = MI_0/\rho, \quad . \quad . \quad . \quad . \quad (3)$$

N is the Weiss molecular field constant,

$$a = \frac{\mu H}{kT} = \frac{\mu NI}{kT} = \frac{N\rho\sigma_M^2}{MRT} \left(\frac{\sigma}{\sigma_0} \right) = \frac{\theta}{T} \left(\frac{\sigma}{\sigma_0} \right), \quad . \quad . \quad (4)$$

θ is the Curie temperature, above which the intrinsic magnetization becomes zero,

$$\theta = \frac{N\rho\sigma_M^2}{MR}. \quad . \quad . \quad . \quad . \quad (5)$$

The connexion between the above quantities and those in Heisenberg's theory may be simply expressed. Let z be the number of neighbouring atoms, J_0 the interchange interaction integral,

$$\left. \begin{aligned} N &= \frac{zJ_0}{2\mu I_0} = \frac{zJ_0 M k}{2\mu^2 \rho R} \\ a &= \frac{2J_0 \sigma}{2kT \sigma_0} \\ \theta &= \frac{zJ_0}{2k} \end{aligned} \right\} \dots \dots \dots (6)$$

It may here be noted that if there are q effective electrons per atom equations (4) and (5) become

$$a = \frac{1}{q} \frac{N \rho \sigma_M^2}{MRT} \frac{\sigma}{\sigma_0}, \dots \dots \dots (4a)$$

$$\theta = \frac{1}{q} \frac{N \rho \sigma_M^2}{MR} \dots \dots \dots (5a)$$

Equation (2), in its second form, remains unchanged,

$$\frac{\sigma}{\sigma_0} = \frac{T}{\theta} a. \dots \dots \dots (2a)$$

For carriers with a j value different from $\frac{1}{2}$, equation (1) is modified ⁽²⁾. For q such carriers per atom (5) becomes

$$\theta = \frac{1}{q} \frac{j+1}{3j} \frac{N \rho \sigma_M^2}{MR} \dots \dots \dots (5b)$$

The consequences of (1) and (2) will now be developed.

Variation of Magnetization with Temperature.—In order to suggest the formal character of the development of the equations, and for brevity, it will be convenient to make use of different symbols, which correspond to those in the magnetic equations in the following way

$$x = 1 - \frac{T}{\theta}, \quad y = \frac{\sigma}{\sigma_0}, \quad u = a. \dots \dots \dots (7)$$

(1) and (2) then become

$$y = \tanh u, \dots \dots \dots (8)$$

$$y = (1 - x) u. \dots \dots \dots (9)$$

The intrinsic magnetization is required as a function of the temperature, that is y as a function of $(1-x)$ or of x . From (8) and (9)

$$(1-x) = \frac{\tanh u}{u} (10)$$

Using tables of $\tanh u$ against u ⁽⁹⁾, values of u (with $\tanh u$) may be found corresponding to an appropriate series

TABLE I.

Calculated Constants for Idealized Ferromagnetic.

$(\tanh u)/u$ $=x'=1-x.$	$u.$	$y=\tanh u.$	$y^2.$	$\frac{dy^2}{dx}=z.$	$\int_0^{x'} \frac{z}{x'} dx'.$
$T/\theta.$	$a.$	$(\sigma/\sigma_0).$	$(\sigma/\sigma_0)^2.$	$S_M.$	$P_E'.$
·1	10·000	1·0000	1·0000	·00	·000
·2	5·000	·9999	·9999	·01	·001
·3	3·325	·9974	·9948	·11	·020
·4	2·464	·9856	·9714	·37	·084
·5	1·915	·9575	·9168	·74	·203
·6	1·512	·9073	·8231	1·16	·374
·65	1·341	·8720	·7604	1·38	·480
·7	1·184	·8287	·6868	1·60	·585
·75	1·034	·7755	·6014	1·81	·705
·8	·888	·7104	·5047	2·04	·828
·85	·741	·6297	·3965	2·28	·962
·9	·584	·5256	·2762	2·52	1·095
·95	·400	·3800	·1444	2·76	1·238
1·0	·000	·0000	·0000	3·00	1·386

The first row gives the formal expressions, the second the corresponding magnetic quantities for the idealized ferromagnetic with one effective electron spin per atom. S_M is the gram atomic specific heat associated with the magnetization. The change in P_E' with T/θ is proportional to the change in thermoelectric power; to obtain the value in volts $\times 10^{-6}$ per degree C., P_E' must be multiplied by 43·44.

of values of $(1-x)$. Values of $\tanh u$ (*i. e.* σ/σ_0) have thus been found for a series of values of $(1-x)$ (*i. e.* T/θ) ranging from 0 to 1. These are shown in Table I. and plotted in fig. 1.

For small values of x (*i. e.* $T/\theta \rightarrow 1$) a series expansion may be obtained for y , or more conveniently for y^2 (*i. e.* $(\sigma/\sigma_0)^2$).

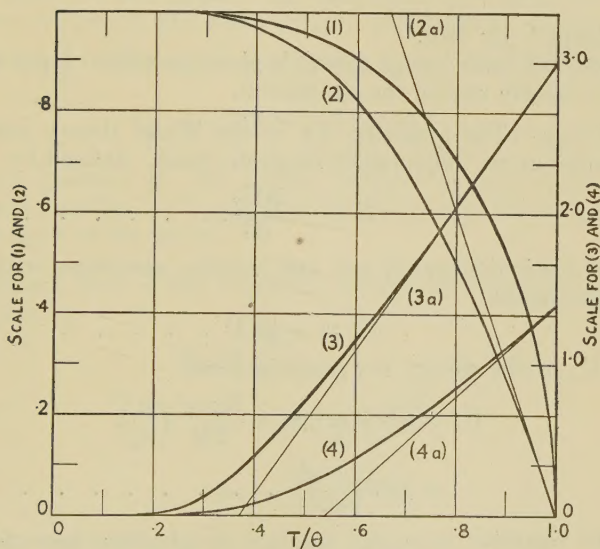
For $u^2 < \frac{1}{4}\pi^2$ ($u < 1.571$)

$$\tanh u = u - \frac{1}{3}u^3 + \frac{2}{15}u^5 - \frac{17}{315}u^7. \quad (11)$$

Using the first three terms in this expansion and (9),

$$\frac{2}{15}u^4 - \frac{1}{3}u^2 + x = 0.$$

Fig. 1.



Variation with Temperature of Intrinsic Magnetization and Associated Properties of Idealized Ferromagnetic.

(1) σ/σ_0 ; (2) $(\sigma/\sigma_0)^2$; (3) Magnetic specific heat, S_M , in calories per gram atom; (4) Variation in thermoelectric power; P_E' is plotted (Eq. 23); (2a), (3a), and (4a) are the tangents at $T/\theta=1$.

From this equation u^2 may be found in terms of x ; squaring both sides of (9), and substituting

$$[y^2]_{x \rightarrow 0} = 3x \left(1 - \frac{8}{10}x \dots\right). \quad (12)$$

Further terms in this expansion are of little value, as the 3-term expansion in (11) is valid only when x is small. From Table I., however, it may be seen that the expansion (12) gives values of y^2 correct to less than 1 per cent. for $x < .4$.

This is illustrated by the following values:—

$$\alpha = \left(1 - \frac{T}{\theta}\right) \quad \begin{array}{cccc} .1 & .2 & .3 & .4 \end{array}$$

$$y^2 = \left(\frac{\sigma}{\sigma_0}\right)^2 \left\{ \begin{array}{l} \text{From (12)} \\ \text{Using tables} \end{array} \right. \quad \begin{array}{cccc} .2760 & .5040 & .6840 & .8160 \\ .2762 & .5047 & .6868 & .8230 \end{array}$$

Thus for $T/\theta > .6$

$$(\sigma/\sigma_0)^2 = 3 \left(1 - \frac{T}{\theta}\right) \left\{ 1 - \frac{8}{10} \left(1 - \frac{T}{\theta}\right) \right\} \quad (12 a)$$

to within 1 per cent.

Over the same range (σ/σ_0) is given to within $\frac{1}{2}$ per cent. by the square root of the expression.

Energy.—The quantity NI in the Weiss theory may be regarded as an “equivalent magnetic field,” defined by

$$H = -\frac{\partial U_v}{\partial I}, \quad \dots \quad (13)$$

where U_v is the energy per unit volume associated with the magnetization

$$U_v = -\frac{1}{2}NI^2 \quad \dots \quad (14)$$

Let U_M be the energy per gram molecule

$$\begin{aligned} U_M &= \frac{1}{2}NM\rho\sigma^2 = -\frac{N\rho\sigma_M^2}{2M}\left(\frac{\sigma}{\sigma_0}\right)^2 \\ &= \frac{1}{2}R\theta\left(\frac{\sigma}{\sigma_0}\right)^2 \quad \dots \quad (15) \end{aligned}$$

The negative magnetic energy at absolute zero (when $\sigma = \sigma_0$) is thus approximately θ calories per gram molecule ($R = 1.986 \div 2$). (Substituting from (6) it will be seen that on the interchange interaction theory this corresponds to a negative energy, when all the spins are parallel, of $\frac{1}{4}zJ_0$ ergs per effective electron.) If there are q effective electrons per atom the energy will be $-\frac{1}{2}qR\theta$. For q effective carriers of mechanical moment j per atom, using (5b), the energy is found to be

$$U_M = -\frac{1}{2}q\frac{3j}{j+1}R\theta\left(\frac{\sigma}{\sigma_0}\right)^2 \quad \dots \quad (15 a)$$

This gives the following values:—

j	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$\rightarrow \infty$
$ U_M _{\text{Max.}}$	$q\theta$	$\frac{3}{2}q\theta$	$\frac{9}{5}q\theta$	$2q\theta$	$3q\theta$

Negative magnetic energy at saturation in calories per gram atom.

A sharp distinction is here shown between the results of the classical theory, in which continuous orientation of the carriers is possible (corresponding to $j \rightarrow \infty$) and the quantum theory, particularly when the "carriers" are electron spins, the one giving an energy at absolute zero three times as great as the other. This will be discussed later in connexion with the experimental results.

A simple geometrical representation of the result may be given. The value of σ/σ_0 may be found graphically from the point of intersection of the line $\sigma/\sigma_0 = (T/\theta)a$, and the curve $\sigma/\sigma_0 = f(j, a)$, where $f(j, a)$ lies between $\tanh a$ and $\coth a - \frac{1}{a}$. The expression for the energy may be written

$$U_M = -qR\theta x \left[\frac{1}{2} \left(\frac{T}{\theta} a \right) \left(\frac{\sigma}{\sigma_0} \right) \right] \dots (15b)$$

The quantity in the square brackets is simply the area bounded by the $a=0$ axis, the line (σ/σ_0) , and the tangent at the origin of the curve.

Specific Heat.—The magnetic specific heat per gram atom is given by

$$\begin{aligned} S_M &= \frac{dU_M}{dT} \\ &= -\frac{1}{2} R\theta \frac{d}{dT} \left(\frac{\sigma}{\sigma_0} \right)^2 \\ &= -\frac{d(\sigma/\sigma_0)^2}{d(T/\theta)} \dots \dots \dots (16) \end{aligned}$$

calories per degree per gram molecule.

For q effective electrons per atom

$$S_M = -q \frac{d(\sigma/\sigma_0)^2}{d(T/\theta)} \dots \dots \dots (16a)$$

Using the formal symbols of (7)

$$S_M = \frac{dy^2}{dx} \dots \dots \dots (16b)$$

The values have been estimated from the y^2 results, and are shown in Table I. and fig. 1.

For x small, from (12)

$$\left[\frac{dy^2}{dx} \right]_{x \rightarrow 0} = 3 \left(1 - \frac{16}{10} x \dots \right) \dots \dots \dots (17)$$

This expression is adequate for $x < .2$, after which the percentage error increases rather rapidly, as may be seen

from a consideration of the errors discussed in connexion with the approximate formula y^2 ,

$x = \left(1 - \frac{T}{\theta}\right)$	·1	·2	·3	·4
$\frac{dy^2}{dx} \left\{ \begin{array}{l} \text{From (17)} \\ \text{From } y^2 \text{ curves} \end{array} \right.$	2·52	2·04	1·56	1·08
	2·52	2·04	1·60	1·16

For $T/\theta > \cdot 8$

$$S_M = 3 \left\{ 1 - \frac{16}{10} \left(1 - \frac{T}{\theta} \right) \right\} (17 a)$$

The slope of the tangent to the $S_M, \frac{T}{\theta}$ curve at $\frac{T}{\theta} = 1$ is

$$\left[\frac{dS_M}{d(T/\theta)} \right]_{T/\theta \rightarrow 1} = 4\cdot 8 (18)$$

Since the total negative energy at absolute zero is θ

$$\int S_M dT = \theta \quad \text{or} \quad \int S_M d(T/\theta) = 1,$$

as is obvious from (16).

This has been used as a check on the values given in Table I. It may be noted that, using the approximate value for S_M given by (17 a),

$$\int_{\cdot 375}^1 S_M d(T/\theta) = \cdot 9375.$$

The difference in the energy at absolute zero and the Curie point is proportional to the area bounded by the S_M curve, the T/θ axis and the ordinate at $T/\theta = 1$ (see fig. 1). The area bounded by the tangent at $T/\theta = 1$ corresponds to over 93 per cent. of this energy (see fig. 1).

Thermoelectric Power.—The fairly sudden change in the Thomson coefficient of a ferromagnetic in the neighbourhood of the Curie point is undoubtedly associated with the change in the intrinsic magnetization. The Thomson coefficient and also the thermoelectric power associated with this magnetization in the idealized ferromagnetic will here be considered. In order to avoid unnecessary numerical factors in the more formal part of the treatment it will be convenient to consider the Thomson coefficient C_E and the thermoelectric power P_E both as referring to the gram electron; C_E is the difference in the specific heat of electricity per gram electron for the ferromagnetic and a substance exactly similar but having no intrinsic magnetization, and P_E is the thermoelectric

power with respect to such a substance. The ordinary thermodynamic argument leads to the relation

$$C_E = T \frac{dP_E}{dT} \quad (19)$$

Let ΔS_M be the change in the specific heat per gram atom due to the addition of one electron; using L for Avogadro's number, C_E may be defined as

$$C_E = L \Delta S_M \quad (20)$$

Now if the addition of one electron results simply in an increase in the number of "free" electrons, ΔS_M will be zero (since S_M is the part of the specific heat associated with the magnetization), unless the magnetization is due to free electrons, a hypothesis which is regarded as untenable. As has been shown elsewhere⁽⁶⁾, however, by an argument similar to that used by Margenau⁽¹⁰⁾ in showing that the number of free electrons is approximately independent of temperature, change of charge does not necessarily result in a change in the number of free electrons. Change in charge may result in a change in the relative numbers of neutral atoms and ions (or of ions in different stages of ionization). Now if in a ferromagnetic the effective electron spins are those of electrons in excess of completed configurations in the ions, addition of an electron will result in an increase in the number of effective spins (and so of the magnetization); if, on the other hand, the effective spins are due to deficiency of electrons, addition of an electron will result in a decrease in the number of effective spins. Now the paramagnetic properties of ions with 25-28 electrons indicate that an increase in the number of electrons is accompanied by a decrease in the effective spin moment. Adopting, then, the simplest hypothesis consistent with these considerations for the idealized ferromagnetic with one effective electron spin per atom (due to a deficient electron), and in which S_M is due to the presence of L such spins,

$$\Delta S_M = -S_M/L$$

$$C_E = -S_M \quad (21)$$

From (19)

$$P_E = - \int_0^T \frac{S_M}{T} dT + K.$$

At $T = \theta$ the intrinsic magnetization disappears and $P_E = 0$,

$$K = \int_0^\theta \frac{S_M}{T} dT,$$

$$P_E = \int_T^{\theta} \frac{S_M}{T} dT, \\ = \int_{T/\theta}^1 \frac{S_M}{(T/\theta)} d(T/\theta). \quad \dots \quad (22)$$

For $T/\theta=0$, the value of this integral is 1.386.

It is to be noted that above the Curie point the thermoelectric coefficients should have "normal" values, the divergence from normality increasing as the temperature decreases below the Curie point (corresponding to the increase in energy associated with the intrinsic magnetization). It is generally more convenient, however, to consider the change in P_E as the temperature increases towards the Curie point, and to write

$$P_E = \int_0^1 \frac{S_M}{(T/\theta)} d(T/\theta) - \int_0^{T/\theta} \frac{S_M}{(T/\theta)} d(T/\theta) \\ = 1.386 - \int_0^{T/\theta} \frac{S_M}{(T/\theta)} d(T/\theta) = 1.386 - P'_E. \quad \dots \quad (23)$$

The values of this second integral P' have been found from the S_M curves; they are given in Table I. and plotted in fig. 1. The units are calories per gram electron per degree C; the most usual experimental units are volts $\times 10^{-6}$ per degree C. When the ordinary conventions are made as to signs⁽⁶⁾, 1 cal. per gm. elec. corresponds to -43.44×10^{-6} volts. With the special assumptions that have been made, the result for the thermoelectric power associated with the magnetization for a ferromagnetic containing one effective electron spin per atom is

$$P_E = -43.44 \left[1.386 - \int_0^{T/\theta} \frac{S_M}{(T/\theta)} d(T/\theta) \right]. \quad (23 a)$$

volts $\times 10^{-6}$ per degree C.

The thermoelectric power of a ferromagnetic with respect to a non-ferromagnetic, otherwise similar, should become increasingly negative as the temperature decreases below the Curie point.

In terms of the formal symbols of (7), (22) may be written in the form

$$P_E = - \int_x^0 \frac{1}{1-x} \frac{dy^2}{dx} dx. \quad \dots \quad (24)$$

For $x \rightarrow 0$ this gives, substituting from (17),

$$P_E = 3x - \frac{9}{10} x^2. \quad \dots \quad (25)$$

This is adequate for $x < .2$.

For $T/\theta > 8$, to within 1 per cent.,

$$P_E = 3\left(1 - \frac{T}{\theta}\right) - \frac{9}{10}\left(1 - \frac{T}{\theta}\right)^2, \quad . \quad . \quad (25 a)$$

and from (19), for the specific heat of electricity,

$$\begin{aligned} C_E &= T \frac{dP_E}{dT} = \frac{T}{\theta} \frac{dP_E}{d(T/\theta)} \\ &= -\left[3 - 4.8\left(1 - \frac{T}{\theta}\right)\right] \quad . \quad . \quad . \quad (26) \end{aligned}$$

The values in (25 a) and (26) are in calories per gram electron per degree, the values in volt $\times 10^{-6}$ per degree being obtained by multiplying by -43.44 .

If there are q effective electrons per atom, on the above assumptions the values for P_E and C_E are unchanged, provided that spin moments only are effective, and that these are independent. This will be discussed in connexion with the experimental results.

The various values which have been calculated in the way indicated are shown in the Table and figure; for temperatures near the Curie point the tabulated values may readily be supplemented by means of the approximate equations (12 a), (17 a), and (25 a).

The Actual Ferromagnetic.

In this section the values calculated for the idealized ferromagnetic will be compared with those observed for nickel, for which the most comprehensive and accurate data are available. The reasons for supposing that electron spins play the part of carriers at ordinary temperatures have been indicated in the Introduction. In nickel there is less than one effective spin per atom, and the calculated results must accordingly be modified where necessary. Let q be the number of effective spins per atom. The low temperature saturation moment is given by Weiss⁽¹¹⁾ as 3380.84,

$$\text{Ni} \quad q = \frac{3380.84}{5593} = .6045.$$

In general q may be taken with sufficient accuracy as .6, corresponding to 3 effective spins in 5 atoms.

It may be noted here that for iron q is greater than 2. Using Weiss's value⁽¹¹⁾ for the saturation moment,

$$\text{Fe} \quad q = \frac{12382}{5593} = 2.214.$$

For cobalt the saturation moment is not known with such accuracy. It is approximately 9 Weiss magnetons per atom,

$$\text{Co} \quad q = \frac{9 \times 1125 \cdot 6}{5593} \doteq 1 \cdot 8.$$

The results for nickel will be compared with those for an idealized ferromagnetic in which there are $\cdot 6$ effective electron spins per atom.

Variation of Magnetization with Temperature.—The theoretical and experimental results have already been compared and discussed by Tyler⁽⁴⁾, so that a brief account only is necessary. The present treatment enables the comparison to

TABLE II.

Intrinsic Magnetization of Nickel. Observed and Calculated Values.

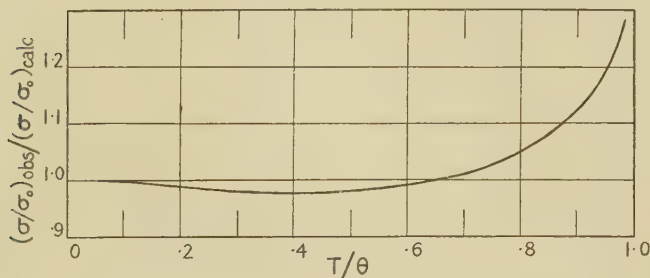
$\frac{T}{\theta}$	σ/σ_0		Obs. Calc.	$\frac{T}{\theta}$	σ/σ_0		Obs. Calc.
	Calc.	Obs.			Calc.	Obs.	
$\cdot 1$	1.0000	$\cdot 997$	$\cdot 997$	$\cdot 7$	$\cdot 8287$	$\cdot 837$	1.01
$\cdot 2$	$\cdot 9999$	$\cdot 991$	$\cdot 99$	$\cdot 75$	$\cdot 7755$	$\cdot 795$	1.03
$\cdot 3$	$\cdot 9974$	$\cdot 979$	$\cdot 98$	$\cdot 8$	$\cdot 7104$	$\cdot 742$	1.05
$\cdot 4$	$\cdot 9856$	$\cdot 961$	$\cdot 975$	$\cdot 85$	$\cdot 6297$	$\cdot 679$	1.08
$\cdot 5$	$\cdot 9575$	$\cdot 937$	$\cdot 98$	$\cdot 9$	$\cdot 5256$	$\cdot 595$	1.13
$\cdot 6$	$\cdot 9073$	$\cdot 895$	$\cdot 99$	$\cdot 95$	$\cdot 3800$	$\cdot 450$	1.19
$\cdot 65$	$\cdot 8720$	$\cdot 870$	1.00	1.0	$\cdot 0000$	$\cdot 000$	—

be made with greater precision. The experimental results used are those of Weiss and Forrer, both for temperatures above^(12, 13) and below (*l. c.*, p. 322)⁽¹¹⁾ room temperature. The values of σ/σ_0 for convenient values of T/θ were obtained by interpolation. θ was taken as 358°C. (631°Abs.).

The calculated and observed values agree to within a few per cent. up to $T/\theta = \cdot 8$. The fact that $\sigma_{\text{obs.}}$ decreases at first more rapidly than $\sigma_{\text{calc.}}$ is, however, undoubtedly significant. Above $T/\theta = \cdot 8$ the ratio of the observed to the calculated values increases rather rapidly. Owing to the peculiarities near the Curie point the observed values close to it are perhaps less reliable as an indication of the true intrinsic magnetization. Taking the values as correct, the ratio appears to rise to a maximum of about 1.28 at $T/\theta = \cdot 98$. The variation of the ratio is shown in fig. 2.

Energy and Specific Heat.—A very careful investigation of the specific heat of nickel between -175°C. and $+460^{\circ}\text{C.}$ has been made by Mme. Lapp⁽¹⁴⁾. The change at the Curie point was found to be $\cdot 037$ (corresponding to $\cdot 037 \times 58\cdot 68 = 2\cdot 17$ calories per gram atom), and this presumably represents the specific heat associated with the change in intrinsic magnetization in the neighbourhood of the Curie point. It is, however, not possible to determine without a certain arbitrariness how the magnetic specific heat varies over the whole range of temperature. This is mainly due to the fact that the apparent atomic heat of nickel above the Curie point is greater than that for non-ferromagnetic metals. Whether this is connected with the magnetic properties is a matter of some doubt, for the atomic heat of all metals at high temperatures exceeds the theoretical

Fig. 2.

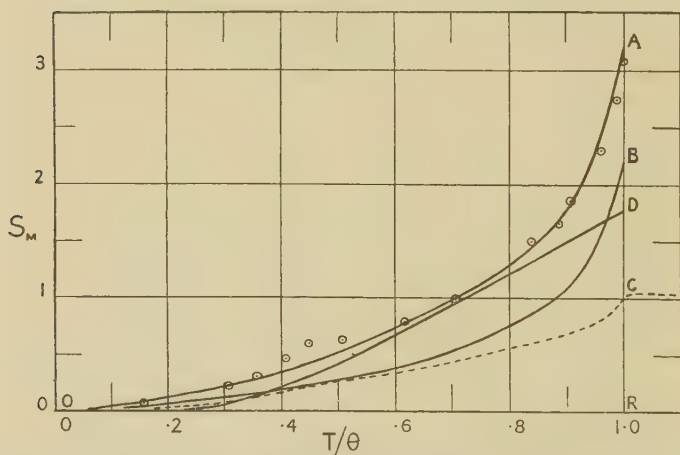
Ratio of Observed to Calculated Value of σ/σ_0 for Nickel.

value $3R$. Mme. Lapp, however, besides correcting the observed specific heat in the usual way for dilatation and for the quantum variation, has also made allowance for this general increasing term (*terme croissant*), taking it to be the same as for copper, a plausible assumption as an approximation. Above the Curie point the atomic heat still exceeds the theoretical value by approximately $\frac{1}{2}R$. The atomic heat over and above that due to the ordinary quantum variation, dilatation, and the increasing term will be denoted by S . This is divided by Mme. Lapp into two parts, S_1 associated with the change in intrinsic magnetization, and S_2 the unknown term (*terme inconnu*) which is presumed to be of magnetic origin. S_1 is calculated by assuming that

$$S_1/A = \frac{1}{2J} n \frac{d\sigma^2}{dT} \cdot \cdot \cdot \cdot \cdot \quad (27)$$

where A is the atomic weight of nickel and n is constant. The values of $d\sigma^2/dT$ are obtained from the results of Weiss and Forrer. When the values of S_1 and $d\sigma^2/dT$ at the Curie point are inserted in this equation, the value of n agrees remarkably well with the value which is appropriate in the Weiss-Curie expression for the variation of the susceptibility of nickel above the Curie point ($n=117,600$). The closeness of the agreement must be regarded as somewhat fortuitous. The assumption of the constancy of n is not entirely arbitrary⁽¹⁵⁾, but by using the equation (27) a correlation of the observed variation of σ^2 and of S_1 is automatically effected and ceases to be significant.

Fig. 3.



Observed and Calculated Specific Heat of Nickel.

(OA) $S_{\text{obs.}}$; (OB) S_1 ; (OC) S_2 ; (OD) $S_{\text{calc.}}$ (See Table III.)

By the procedure adopted any experimental errors make their appearance in S_2 , where small relative errors in the specific heat determinations appear relatively large. Mme. Lapp considers that it is not possible to be certain whether the rather erratic variations in S_2 are real or not.

In Table III. are given the values of S_1 and the smoothed values of S and S_2 derived by interpolation from Mme. Lapp's results. (In fig. 3 a few of the observed values for S are given to indicate roughly the order of magnitude of the variations) The calculated values for S are obtained by multiplying the values of S_m in Table I. by $\cdot 6$ (corresponding to $q=\cdot 6$).

In detail there is little agreement between the calculated curve (OD) and the curve either for S (OA) or S_1 (OB). It is noticeable, however, that the calculated and observed S-curves do not differ greatly below $T/\theta = \cdot 8$, and over the whole range the differences are such as to be obviously connected with the differences in the observed and calculated values of the magnetization.

Energy.—From the specific heat curves information can be obtained as to the difference in energy at absolute zero and the Curie point, and this in some ways, as has been

TABLE III.

Observed and Calculated Specific Heat of Nickel
(calories per gram atom).

T/ θ .	S _{obs.}	S ₁ .	S ₂ .	Sealc.	T/ θ .	S _{obs.}	S ₁ .	S ₂ .	Sealc.
·1	·05	·04	·01	·00	·8	1·31	·74	·57	1·20
·2	·13	·08	·05	·01	·85	1·50	·87	·63	1·37
·3	·24	·13	·11	·07	·9	1·76	1·08	·68	1·51
·4	·36	·18	·18	·22	·95	2·25	1·48	·77	1·66
·5	·53	·26	·27	·44	1·0	3·20	2·20	1·00	1·80
·6	·74	·38	·36	·70	1·05	1·07	0	1·07	0
·7	1·00	·53	·47	·96	1·1	1·06	0	1·06	0

The values of S_{obs.} and S₂ are smoothed. S₁ and S₂ are Lapp's magnetic and unknown terms, such that $S_1 + S_2 = S_{obs.}$

indicated, is of more value from a theoretical point of view than a knowledge of the magnetic specific heat at one particular temperature. Unfortunately the same difficulties arise as before in connexion with the unknown term. The difference of energy, corresponding to the negative energy at absolute zero, must, however, lie between the values represented by the areas OAR, and OBR. This gives the result

$$\cdot 76 \times \frac{1}{2} R\theta > |U_M| > \cdot 44 \times \frac{1}{2} R\theta \dots (28)$$

(Weiss⁽¹⁵⁾, in discussing these results, gives the areas in the same units as ·76 and ·43.) This has to be compared with the theoretical result for ·6 effective electron spins per atom (see equation 15.a)

$$|U_M| = \cdot 6 \times \frac{1}{2} R\theta \dots (29)$$

Thermoelectric Power.—The most precise results at present available are those of Dorfman and Jaanus⁽¹⁶⁾ for nickel, against platinum, over a range from about 310° C. to 460° C. For two specimens they deduce from the change of slope at the Curie point of the thermoelectric power curves values for the change in the specific heat of electricity of 4.8 and 4.7×10^{-24} calories per degree per electron, corresponding to 2.91 and 2.85 calories per gram electron. These agree closely with the theoretical value 3.0⁽⁶⁾ (equation 21 and Table I.). In view of the disagreement between the theoretical values for the idealized ferromagnetic and the observed values for nickel for the specific heat and magnetization near the Curie point, the close agreement here cannot be accepted at its face value. An extension of the comparison over a range of temperatures is desirable. The determination of the Thomson coefficient involves the determination of the slopes of the thermoelectric power curves, which have to be slightly extrapolated from above and below in the neighbourhood of the Curie point. It would be more satisfactory if a comparison could be made between the theoretical thermoelectric power curves (which can be determined with precision) and those observed. The experimental curves are those of nickel with respect to platinum ($_{\text{Ni}}P_{\text{Pt}}$); and from the results the value of $P_{\text{obs.}}$ may be directly obtained where

$$P_{\text{obs.}} = (_{\text{Ni}}P_{\text{Pt}})_T - (_{\text{Ni}}P_{\text{Pt}})_{\theta} \quad . \quad . \quad . \quad (30)$$

This quantity, however, is not necessarily comparable with $P_{\text{calc.}}$, for $P_{\text{calc.}}$ gives the thermoelectric power of nickel with respect to a substance exactly similar except that it has no intrinsic magnetization. Above the Curie point, according to Dorfman's results, $_{\text{Ni}}P_{\text{Pt}}$ is approximately constant, and this would seem to justify an extrapolation which would render $P_{\text{obs.}}$ and $P_{\text{calc.}}$ comparable. More recent experiments of Grew⁽¹⁷⁾, however, have shown that just above the Curie point there are peculiarities in the thermoelectric behaviour, and that at higher temperatures the thermoelectric power varies with temperature. This should be borne in mind in connexion with Table IV., which gives $P_{\text{obs.}}$ as above defined and $P_{\text{calc.}}$. Over the range of temperatures involved $P_{\text{calc.}}$ may be obtained from (25 a). At a temperature $T < \theta$, P_{E} is positive, and P negative with respect to the value at $T = \theta$. P is expressed in the usual experimental units, volts $\times 10^{-6}$ per degree.

The sign and order of magnitude of the effect is correctly given by the theory⁽⁶⁾. Before a more detailed comparison can be made, experimental results for a greater range of

temperatures are necessary. It seems very unlikely, however, that the "normal" variation with temperature of the thermoelectric power of nickel with respect to platinum is sufficient to account for the difference between the experimental and calculated curves. The Thomson coefficient (with the same reservations as before) is given by the slope of the curves

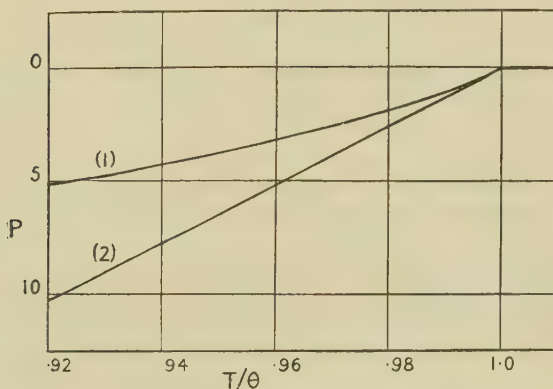
TABLE IV.

Observed and Calculated Thermoelectric Power for Nickel.

$\frac{T}{\theta}$	$-P_{\text{obs.}}$	$-P_{\text{calc.}}$	$\frac{T}{\theta}$	$-P_{\text{obs.}}$	$-P_{\text{calc.}}$
1.00	0.0	0.00	.95	3.7	6.42
.99	1.1	1.30	.94	4.2	7.68
.98	1.8	2.61	.93	4.7	8.90
.97	2.6	3.91	.92	5.1	10.2
.96	3.2	5.19	.91	—	11.4

$P_{\text{obs.}} = (NiP_{Pt})_T - (NiP_{Pt})_{\theta}$. Units 10^{-6} volt per degree C.

Fig. 4.



Observed and calculated thermoelectric power curves for nickel.

(1) $P_{\text{obs.}} = (NiP_{Pt})_T - (NiP_{Pt})_{\theta}$.

(2) $P_{\text{calc.}}$

Units 10^{-6} volt per degree C.

multiplied by T/θ . Over the range of temperature covered by the experiments the "observed" value is about equal to that calculated at the Curie point, and falls to a value less than half that calculated at $T/\theta = .9$.

Discussion.

General.—The comparison of the experimental results for nickel with those calculated theoretically shows that the idealized ferromagnetic is fairly satisfactory as a first approximation to the actual ferromagnetic. This is shown in particular by the general agreement of the magnetization curves below about $T/\theta = \cdot 8$, and by the results for the energy associated with the intrinsic magnetization. The agreement is certainly much closer than that obtained by assuming the carriers to have a j value different from $\frac{1}{2}$. There are, however, significant disagreements, on which stress has been laid, both at low temperatures and at temperatures approaching the Curie point. The low temperature deviations will not here be considered. The relative difference in the observed and calculated magnetization (σ/σ_0) is small (see fig. 2), but the difference in the variation of $1 - (\sigma/\sigma_0)$ with temperature at low temperatures is considerable. It may be possible to account for this low temperature variation by a development of Heisenberg's theory somewhat similar to that given by Bloch⁽¹⁸⁾, but up to the present the experimental results have not been satisfactorily accounted for.

At temperatures approaching the Curie point the divergence between the calculated and observed values becomes large (see figs. 2 and 3). On the theoretical side it becomes necessary to examine the modifications indicated by a fuller consideration of the principles underlying the justification of the idealized "model" chosen as a first approximation.

The ferromagnetic metal is treated as an aggregate of atoms, ions, and free electrons, the atoms or ions, if they contain incomplete groups of electrons, having a magnetic moment associated with them. Widely dispersed constituents of this kind would form a paramagnetic gas, obeying Curie's law; aggregation, accompanied by increasing interaction, may result in the formation of a paramagnetic obeying the Curie-Weiss law, a ferromagnetic, or a substance which is neither a normal para- nor dia-magnetic. The special characteristic of the interacting atoms and ions of the ferromagnetic elements is that the incomplete groups of electrons in them are those belonging to the highest quantum group, so that strong interaction may occur between the effective magnetic groups of electrons in them, and also that the electron groups are incomplete in the sense of containing more than half and less than the whole of the number of electrons required to complete the particular group. (In this sense the effective electrons may be referred to as "missing electrons.")

The number of free electrons, as shown by Margenau⁽¹⁰⁾, may be taken as approximately independent of temperature. The justification for this may be briefly indicated. Considering a metal as an equilibrium distribution of neutral atoms, ions, and free electrons, let ϕ_A be the negative energy of an electron bound in an atom, ϕ_0 the negative energy of a free electron inside the metal with respect to that of one outside, and ϵ_0 the maximum kinetic energy of the free electrons. Then, for equilibrium,

$$\phi_A = \phi_0 - \epsilon_0. \quad . \quad . \quad . \quad . \quad . \quad (31)$$

For a given number of free electrons ϵ_0 is practically independent of temperature (over ordinary ranges), so that unless ϕ_A and ϕ_0 vary considerably—there is no reason for supposing that they do—the number of free electrons will remain approximately constant.

Ferromagnetism must be attributed to the interaction of the incomplete atoms or ions. Now in a free atom or ion the individual electron orbital moments may be regarded as combining to give a resultant l , the spin moments to give a resultant s , and l and s to give a resultant j . When there are strong fields, however, or strong interaction, the l and s moments may be regarded as independent. In ferromagnetics it seems as if the interaction between the spins of electrons in neighbouring atoms may become comparable with the ordinary interaction of spins in a single atom. The order of magnitude of the different types of interaction will next be considered.

It may be noted that the process here adopted is to take the aggregate of quasi-individualized atoms, ions, and electrons as the starting point, the appropriate interactions between them then being introduced; if a different starting point were taken—say an aggregate of neutral atoms—the introduction of the then appropriate perturbations should lead to the same final result.

Magnitude of Interaction Effects.—For the present purpose it is sufficient to consider the simple vector model of the atom. The interaction between the orbital moments of the electrons may be taken as sufficiently great to justify the use of the symbol l to represent the resultant orbital moment of the atom as a whole. The spins, however, must be considered individually. The symbol ss will be used to indicate the interaction between the spins in a single atom, ss' that between the spins of neighbouring atoms. The symbols ls and ls' ($=sl'$) are also required.

It is the interaction between neighbouring spins which is primarily responsible for ferromagnetism. When $\sigma/\sigma_0=1$ the negative energy associated with each effective electron spin is $\frac{1}{2}k\theta$ (see equation 15). For the equivalent effective magnetic field

$$H = \frac{k\theta}{2\mu_B} = \frac{1.372 \times 10^{-16}}{2 \times 9.23 \times 10^{-21}} \theta = 7.4 \times 10^3 \theta. \quad (32)$$

Thus the effective field equivalent to the ss' interaction may be readily calculated. For nickel, $\theta = 631$,

$$\text{Ni} \quad ss' \quad H = 4.7 \times 10^6 \text{ gauss.}$$

(For Fe, $\theta = 1040$ gives $H = 7.7 \times 10^6$ gauss).

A rough estimate of the order of magnitude of other interactions may be made from the data for the low energy levels of iron (due to Russell) quoted by Powell⁽¹⁹⁾,

Fe	⁵ D	⁵ F	³ F
	0-978	6928-8155	11976-12969.

Since a quintet term corresponds to 4 parallel spins, and the wave number range ($\doteq 1000$) corresponds to the difference of energy when these are parallel and antiparallel to l , for the effective field corresponding to the ls interaction, in this case

$$ls \ (l=2) \ H = \frac{ch\Delta\nu}{8\mu_B} = \frac{2.13 \times 10^4}{8} \Delta\nu = 2.6 \times 10^6 \text{ gauss.}$$

Similarly, the mean difference in the ^5F and ^3F terms may be taken as giving approximately the difference in the energy associated with 4 parallel spins (6 pairs) and 2 parallel spins. For the effective field on each electron corresponding to the spin interaction of a pair, the result then is

$$ss \quad H \doteq \frac{2.13 \times 10^4 \times 5000}{10} \doteq 1.06 \times 10^7 \text{ gauss.}$$

The effective field associated with the ss' interaction is greatest when the spins are parallel and decreases to zero at the Curie point, being proportional to $(\sigma/\sigma_0)^2$. The ll' interaction must be supposed large (of the same order of magnitude as the ll interaction), though the effectiveness of the equivalent field will decrease with increasing temperature. This has been discussed in connexion with the paramagnetism of the ions of the first transition series⁽²⁰⁾. A similar result will hold for the smaller ls' interaction. It may be noted that the effect of the ll' interaction is to maintain a non-magnetized state as far as the orbital moments are concerned. The equivalent field may be regarded as one distributed at

random, or in some way symmetrically related to the crystal axes, and varying from atom to atom. It has been shown by Powell⁽¹⁹⁾ that problems connected with the direction of magnetization of single crystals may be interpreted by introducing a crystalline field which arises from the ls interaction (or, with the above symbolism, the ls and ls' interactions).

The important point indicated by the above estimates is that when the magnetization is near saturation, the ss' interaction in ferromagnetics is of the same order of magnitude as the ss interaction. This provides the justification for regarding the spins as independent in a first approximation. With the decrease in magnetization as the Curie point is approached, however, the effective ss' field decreases, and since the effective ss field remains constant, the state is approached in which it is more appropriate to consider the resultant spin moment of the atom as a whole rather than that of the individual electrons. This will not affect the results for Ni, but for Co and Fe in which there is more than one effective spin per atom, it will become more important. There is, however, another effect. The ls interactions become relatively more important, and, as the temperature rises, the ll' interactions become less important. Superposed on the ferromagnetic effect there will therefore be an effect corresponding to a change in a paramagnetic from a state in which the Weiss magneton number is $5\sqrt{4s(s+1)}$ to one in which it is $5\sqrt{4s(s+1) + l(l+1)}$, the intermediate state being that in which the l moment is only partially effective.

These considerations suggest why the Weiss magneton value obtained from the susceptibility above the Curie point and that obtained at low temperatures differ, even when the ordinary quantum effects are taken into account. They also shed some light on the divergencies between the observed variation of magnetization and specific heat and that calculated by assuming that independent electron spins only were involved. At present it does not seem possible to determine what would be the spectroscopic state of the atoms and ions in a ferromagnetic, if free; and for that reason only a brief qualitative discussion of the various effects will here be given.

Susceptibility above the Curie Point.—For nickel the simplest hypothesis to make is that of five atoms in the solid, three, if free, would be in a $^2D_{5/2}$ state, and two in a $^1S_0$ state. For the Weiss magneton value p

$$5\sqrt{4s(s+1)} < p < 5\sqrt{4s(s+1) + l(l+1)}.$$

For the ${}^2D_{5/2}$ state, $s = \frac{1}{2}$, $l = 2$,

$$6.66 < p < 11.53.$$

The observed values for p are 8.02 (420° – 900° C.) and 8.96 (900° C.—), indicating a partially effective l moment.

It is interesting to compare the results for iron. Four atoms in a state ${}^3F_4$ and one in a state ${}^4F_{9/2}$ may be assumed (corresponding to the states of ions with 26 and 25 electrons, and to the observed low temperature saturation moment). Independent spins give $p = 12.7$, resultant spin moments 15.3 , and resultant spin and orbital moments 23.0 ; the observed value for p ($Fe\beta_1$) is 20.9 .

A transition from a state in which only spin moments are effective to one in which orbital moments are also partially effective, is clearly indicated. The "problem of the two Curie points" is possibly connected with the occurrence of a stage in this transition.

Magnetization.—The salient fact which has to be explained is that the ratio of the observed to the calculated magnetization for nickel increases above $T/\theta = .8$ to a value of about 1.3 (see fig. 2); this may be attributed to an increase in the effective saturation moment σ_0 at absolute zero to σ'_0 , σ_0 being due to the electron spin, σ'_0 to this and the partially effective l moment. Taking the ${}^2D_{5/2}$ state

$$\frac{\sigma'_0}{\sigma_0} = \frac{1 + \phi l}{1}.$$

The value of ϕ above the Curie point may be obtained from the equation

$$5\sqrt{\frac{3}{5}\{4s(s+1) + \phi l(l+1)\}} = 8.02$$

where $s = 0$, $l = 2$.

This gives $\phi = .211$, and $\phi l = .422$.

Thus $\sigma'_0/\sigma_0 = 1.42$.

This value is compatible with the gradual increase from 1.0 at $T/\theta = .7$ to about 1.3 at $T/\theta = 1$. A general explanation is thus obtained of the form of the experimental magnetization curves.

Energy and Specific Heat.—The value of $\int S_M dT$ from absolute zero to the temperature at which intrinsic magnetization disappears is equal to the negative energy associated with the magnetization at absolute zero. When interactions other than that between the spins play a part in determining

the magnetization, both the variation of the magnetization with temperature and of the energy associated with it will differ from that calculated on the pure spin interaction basis. The specific heat will be smaller than that calculated when the magnetization varies more slowly, and greater when it varies more rapidly; but it is not legitimate to assume that it varies strictly as $d\sigma^2/dT$, as has been done by Weiss⁽¹⁵⁾ and Lapp⁽¹⁴⁾, for the ratio of the effective equivalent field and the magnetization will depend on the exact character of the interaction. If it were possible to separate exactly the part of the specific heat connected with the intrinsic magnetization, it should vary with temperature in such a way as to keep the value of $\int_0^\theta S_M dT$ unchanged. The observations support this view and indicate that it is electron spin which is effective at low temperatures. (See equations 28, 29, 15.) The difficulty in connexion with the high specific heat above the Curie point, however, is unexplained, and at present prevents a more precise treatment. It may be that this high specific heat is connected with changes in the energy associated with other interactions.

Thermoelectric Power.—The basis of the treatment of the thermoelectric power (and of the Thomson coefficient) associated with magnetization is that change of charge results in a change in the relative numbers of atoms and ions (or of ions in different stages of ionization) and not in a change in the number of free electrons⁽⁶⁾. When addition of an electron changes an ion from a state in which $j=\frac{1}{2}$ to one in which $j=0$, the specific heat of electricity per gram electron at (or just below) the Curie point is equal to -3 . (It is equal to the change in the specific heat S_M due to the addition of one electron, multiplied by Avogadro's number. See equation 20.) For the idealized ferromagnetic previously considered

$$C_E = - [(S_M)_{j=\frac{1}{2}} - (S_M)_{j=0}] \dots \dots \dots (33)$$

where S_M is the specific heat at the Curie point.

The general expression for S_M is (*l. c.* equation 35)²

$$S_M = \frac{5R}{2} \frac{j^2 + j}{j^2 + j + \frac{1}{2}} \dots \dots \dots (34)$$

Now at the Curie point the evidence discussed shows that the electron spins can no longer be regarded as independent. The effective value of j may differ from $\frac{1}{2}$ owing to the l moments becoming partly effective, or to the individual s moments continuing to give a resultant s for the atom as a

whole. For illustrative purposes the following values are calculated from (33) and (34) :—

$$\begin{aligned} j = \frac{1}{2} \rightarrow 0 & \quad C_E = -(R/2) \times 3. \\ j = 1 \rightarrow \frac{1}{2} & \quad C_E = -(R/2) \times 1. \\ j = 1\frac{1}{2} \rightarrow 1 & \quad C_E = -(R/2) \times 0.41. \end{aligned}$$

These values are sufficient to show how values for C_E differing from 3 may occur, though a much fuller consideration of the interactions would be necessary in a detailed treatment. Further experimental results for nickel and other ferromagnetic metals over wide ranges of temperature will be of great interest.

Summary.

The relation of the intrinsic magnetization to other properties of ferromagnetics is briefly discussed, and evidence for regarding ferromagnetism at ordinary temperatures as due to the interchange interaction of electron spins is summarized.

Values are calculated for the variation with temperature over the whole range from absolute zero to the Curie point, θ , of the magnetization, and the associated specific heat and thermoelectric power of an idealized ferromagnetic (fig. 1, Table I.). The "idealized ferromagnetic" is one in which the magnetic properties are due entirely to electron spin interaction. The calculations are made for one effective spin per atom, and the modifications when there are q effective spins per atom, and when the carriers have a mechanical moment j differing from $\frac{1}{2}$ are indicated.

The observed characteristics of nickel are compared with those of the idealized ferromagnetic for which $q=6$, the comparison being shown in Tables II.–IV. and figs. 2–4. Except for slight deviations at low temperatures there is fair agreement up to about $T/\theta=8$. Above this, as T approaches θ , the ratio of the observed to the calculated magnetization increases up to about 1.3. The rate of change of the specific heat is also considerably greater than that calculated. The calculated total change of energy between 0 and θ , however, falls within the experimental limits. The observed specific heat of electricity at θ is of the same sign as that calculated, and agrees closely in magnitude, but the change in the thermoelectric power (with respect to platinum) between $T/\theta=1$ and .9 is about half that calculated.

It is shown that a correlation of the properties above and below θ , and a more complete interpretation of the properties

below θ , can be given by taking into account interactions other than those between the spin moments. When the magnetization approaches saturation, the effective field corresponding to the interaction of spins in neighbouring atoms (ss') is of the same order of magnitude as that between spins in the same atom (ss). As the magnetization falls off, the effect of the ss' interaction decreases.

At higher temperatures the magnetic properties may be interpreted in terms of a resultant spin moment for the atom as a whole, and a partially effective orbital moment. There is a gradual change to this state from the state occurring when the intrinsic magnetization is large in which separate spin moments in each atom or ion can be treated as individually effective.

The susceptibility above θ , and the intrinsic magnetization, specific heat, and thermoelectric power below θ are discussed, and a qualitative interpretation is given of the differences between nickel and the idealized ferromagnetic.

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LXXV. *The Coupled Duplet and Octet.*

By ANTHONY FELIX RICHTER*.

ACCORDING to H. G. Grimm's⁽¹⁾ distribution of the distinctive groups of electrons we classify them into three classes.

The first class contains the duplet of helium ($n_{\max.}=1$, $k=1$) and the octet of the other rare gases ($n_{\max.}\geq 2$, $k=1$, and 2). These groups of the first rank of stability can be obtained by giving off or by taking up of electrons.

To the second class we assign the group of eighteen which is represented in the periodic system by the diamagnetic nickel⁽²⁾ (2, 8; 4, 6), palladium, and platinum. These groups are not stable enough, but become stable by increasing the central charge by two. Therefore they cannot be obtained by the taking up of electrons.

The third class contains the remaining configurations ("Restkonfigurationen"), *i. e.*, stripped atoms, on the surface of which there are subgroups or grouplets and, besides this, the configurations of the ions of the transition elements.

As a base for the distribution of electrons, especially of the valency electrons, the scheme proposed by H. Lessheim and R. Samuel⁽³⁾ is chosen. This modification of the Bohr-Stoner's distribution of the valency electrons has been warmly received by the atomic chemists, *e. g.*, T. M. Lowry⁽⁴⁾, and supported by the author⁽⁵⁾, in discussing the curve of the ionization potentials. Assuming that the ions reach the configurations of the preceding neutral atom in the period, the statement of Lessheim and Samuel about the reorganization of the remaining configurations appears to be only a consequence of that assumption⁽⁶⁾.

The origin of the grouplet n_{11} and of the pair of shared electrons is, according to G. N. Lewis⁽⁷⁾, due to the neutralization of the magnetic moments of the paired electrons. The neutralization of the moments of the shared electrons as well as of the grouplets, *i. e.*, the tendency to covalency, is supported by the increase of the action of the central charge. Thus dissociation work increases as a result of the increasing action of the central charge, for example :

$$D_{K_2} = 15.5 \text{ cal.} \quad D_{Na_2} = 23.8 (30) \text{ cal.} \quad D_{H_2} = 106.7 \text{ cal.}$$

If the outer shell has lost something of its stability, *i. e.*, of its degree of neutralization and consequently of its screening power, the mutual neutralization with the *following* grouplet

* Communicated by the Author.

n_{11} causes a stronger coherence of these groups than usual. The groups are *coupled*. The tendency to covalency rises then to such an amount that it can compete with electrovalency.

This coupling accounts for the nearly precious character of mercury as well as for its covalency.

$X^- \text{Hg}_2^{++} X^-$ is known even in an aqueous solution.

But the coupled duplet of mercury is not stable enough; two atoms (Hg_2) can be held together by their mutual polarization.

It is, according to G. N. Lewis, neither necessary nor expedient to assume the total mutual elimination of moments of a pair of electrons; we suppose rather that there exists a residual magnetic field emanating from the pair.

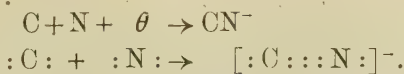
The great stability of the octet is probably due to the optimum steric and energetic conditions for neutralizing the residual magnetic field. The singular importance of the octet of the rare gases is due to the coincidence of the electrical and magnetic neutralization.

Having regard to the coupling of the motion of the centre of gravity of the electrons and of their spin, H. Lessheim⁽⁸⁾ pointed out the exceptional place of the rare gases also in the undulatory theory.

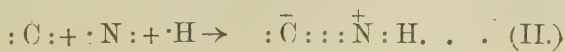
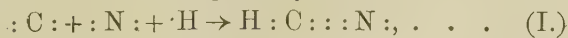
But the degree of stability of the octet can be lowered to a certain degree. This happens, *e. g.*, in the octet of radon, in consequence of the lanthanide-contraction. The outer group of eighteen has lost extraordinarily much of its stability, so that it couples at least with the grouplet 6_{11} and causes a distortion of the octet.

The octet, built up either by electrovalency or by covalency, can also, in consequence of the insufficient neutralization, couple with the group of two or eight so as to give a *coupled duplet* or a *coupled octet*.

This coupled duplet can be attained by taking up one electron ($=\theta$):



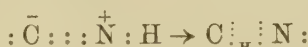
We can also imagine an immediate neutralization of five duplets instead of one duplet and one octet, the result being the same. But in our instance we must imagine the coupling taking place between the octet and the duplet as the duplets $\text{C}:\text{H}$ and $\text{N}:\text{H}$ are not energetically identical.



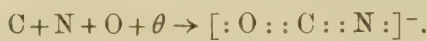
The triple bond of the iso-form of prussic acid (II.) is supported by the spectroscopic study of A. Dadien⁽⁹⁾.

When combining, the elements tend to satisfy successively their negative tendency; if this cannot take place, the molecule is "unsaturated" and strives to compensate this unsaturation by conjugation.

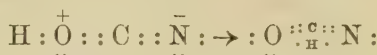
Thus



The coupling of the octets explains the reactions:



For O we can substitute S, Se, Te. The unsaturated state of the molecule, especially when we imagine the hydrogen to be attached to a lone pair of the oxygen, is compensated by the conjugation:



The isomeric fulminic acid has the formula

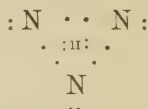


Between nitrogen and oxygen there is no difference in the charge, except that caused by the shifting of the octet.

A further instance is the reaction:



The conjugated N_3H molecule could be formulated, perhaps, as follows:—

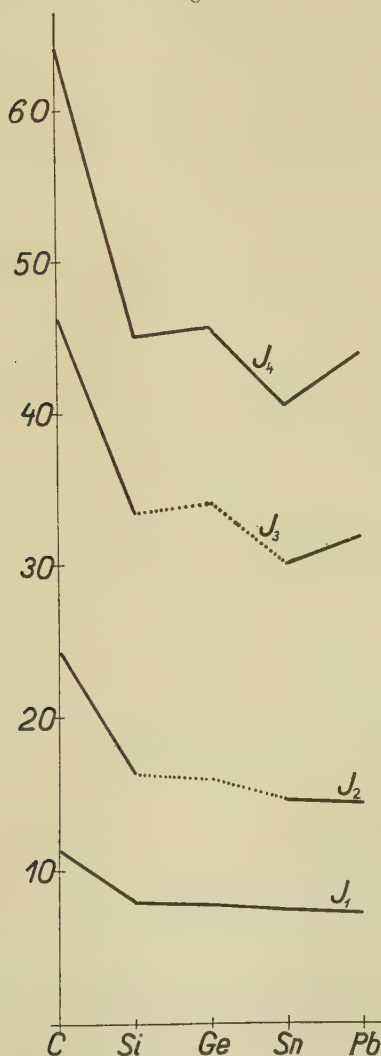


The experimental evidence for the idea of coupling of distinctive groups is given by the curves of ionization potentials. The ionization potentials decrease, as known in the column of homologous elements, with increasing radius, of course if the coupling of residual moments does not take place.

This can explain the higher ionization potentials of radium as compared with barium (because the octet of radon is coupled with the grouplet 6₁₁), and especially that of mercury as compared with cadmium (because the duplet is coupled with the group of eighteen). If this coupled group

becomes *stable* by increasing the central charge by two⁽¹⁰⁾, the electrons surrounding it will be removed easier, their

Fig. 1.



The curves of the 1st-4th ionization degree.

ionization potentials diminishing again with the increase of the atomic radius. This is illustrated by the graph

representing the curves of the ionization potentials within the fourth column of the periodic table. Just the same is apparent, though to a less degree, in the stabilized coupled group of zinc (I_3 and I_4 of germanium and lead compared with those of silicon and tin).

Finally, I would direct the attention to the coupling of two paramagnetic compounds NO and $[\text{Fe}(\text{CN})_6]\text{K}_3$ (resp. $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]\text{K}_3$), to the diamagnetic compound $[\text{Fe}(\text{CN})_5\text{NO}]\text{K}_3$, which is clear evidence of the neutralization of the electronic groups in the molecule itself.

Summary.

The degree of stability of distinctive groups is due mainly to the neutralization of mechanic and magnetic moments.

The neutralization of residual moments leads to coupled systems.

The coupling of systems is able to explain the characteristic course of the curves of the ionization potentials and of the chemical properties of the elements concerned.

References.

- (1) *Zeits. f. phys. Chem.* xcvi. p. 353 (1921).
- (2) L. R. Ingersoll, *Phys. Rev.* xxv. p. 114 (1925).
- (3) *Zeits. f. Physik*, xl. p. 220 (1927); xlii. p. 614 (1927).
- (4) 'Nature,' cxxiii. p. 571 (1929).
- (5) *Zeits. f. phys. Chem.* B vi. p. 111 (1929).
- (6) A. F. Richter, 'Spisy Lékařské Fakulty Masarykovy University,' viii. p. 99 (1930).
- (7) G. N. Lewis, "Valence and Structure of Atoms and Molecules," Amer. Chem. Soc. Monogr. Ser. 1923.
- (8) *Zeits. f. Physik*, li. p. 828 (1928).
- (9) A. Dadiou, *Naturwiss.* xviii. p. 895 (1930).
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November 1930.

LXXVI. *Three Different Effects of Conjugation.*

By A. F. RICHTER *.

WHEN a certain group (of electrons or of atoms) is in a condition of unsaturation, it strives against its state by conjugating with another similar group. According to

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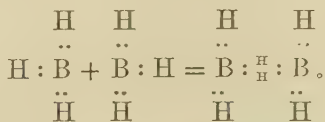
the nature of the unsaturated group whose conjugation we are considering, we distinguish between an intra-atomic, an innermolecular, and extramolecular conjugation.

The conception about the mutual neutralization of the residual moments of the groups of electrons has been developed in my last paper ⁽¹⁾. The groups of electrons which are not stable enough can be considered as unsaturated; then we can call the mutual neutralization between these groups and the following coupling an *intra-atomic conjugation*. The experimental evidence for this conjugation is given by the curves of ionization potentials and by nearly precious character of certain heavy elements.

The innermolecular conjugation is one which is generally known and studied by organic and atomic chemists. In this connexion I may refer to the monographs of H. Kaufmann ⁽²⁾, of G. N. Lewis ⁽³⁾, and of F. Ephraïm ⁽⁴⁾.

When a molecule is in condition of unsaturation and an innermolecular conjugation cannot occur, it tends to conjugate with another molecule, the tendency and possibility of conjugating being dependent upon the degree of unsaturation and upon the *presence* of hydrogen nuclei.

Thus a borine molecule—having an uncomplete octet—conjugates with another molecule so as to form a new conjugated molecule and to complete its octet:

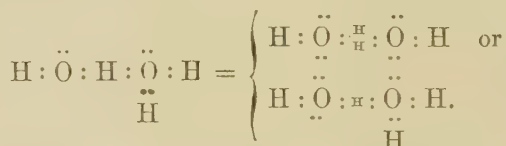


The conjugative bond is naturally looser than a usual covalency. It can be effectuated only by the electronless proton, which becomes common to the shared atoms (kernels). When all three hydrogen atoms are replaced by the methylic radicals, for instance, then the trimethylborine loses its conjugative faculty, although the combining with compounds with a lone pair of electrons is the best evidence of a persisting and strong unsaturation.

This *function principle*, in explaining the so-called borine bond, permits us to do without any special premise, which is to be made in order to explain the borine bond. Thus the negative quinquivalency with the extrapolation of the Hückel-Grimm's law ⁽⁵⁾, the action even of the K-electrons assumed by Eastman ⁽⁶⁾, E. Müller ⁽⁷⁾, and last, in a new fashion, by W. Hellriegel ⁽⁸⁾, the assumption of coordination number 4, can be given up in explaining the borine bond and be replaced by the conjugation.

A further example of an extramolecular conjugation we can see in the association of the pseudoatoms, which phenomenon has been described and explained by the assumption of bivalent hydrogen by G. N. Lewis⁽³⁾. ("It is a striking fact that the liquids whose behaviour indicates a large measure of association and which have the high dielectric constant and ionizing power which seems to be an accompaniment of this association, are *compounds* which contain *hydrogen as well as a lone pair of electrons*.")

In assuming the conjugative bond (we do not consider in this connexion the polarization of the molecules as a reason for combining) instead of a bivalent hydrogen, we can modify his writing of reactions as follows:—



The proton belongs at a given moment only to two shared electrons.

The formal coincidence may be pointed out of the given formula



which I tried to support by the function reason with the formula of A. F. Core⁽⁹⁾.

The logical economy of the premise and its large application for the seemingly most different phenomena are its advantages.

References.

- (1) A. F. Richter, *Phil. Mag.* xii p. 764 (Oct. 1931).
- (2) H. Kaufmann, 'Die Valenzlehre,' 1911.
- (3) G. N. Lewis, 'Valence and Structure of Atoms and Molecules,' 1923.
- (4) F. Ephraim, Ostwald-Drucker-Walden: *Handb. d. allgem. Chem.* vol. vi. *Chemische Valenz- und Bindungslehre*.
- (5) E. Wiberg, *Zeits. f. anorg. und allgem. Chem.* clxxix. p. 309 (1929); *Helv. chim. acta* xii. p. 225 (1929).
- (6) Cited from G. N. Lewis (3).
- (7) E. Müller, *Zeits. f. Elektrochemie*, xxxi. p. 332 (1925).
- (8) W. Hellriegel, *Zeits. f. anorg. und allgem. Chem.* clxxxv. p. 65 (1930).
- (9) A. F. Core, *Journ. Soc. Chem. Ind.* xlvi. p. 642 (1927).

Chemistry Laboratory of
Charles's University, Prague.
April 27th, 1931.

LXXVII. *The Behaviour of Conical Diaphragms used in Acoustic Apparatus for the Reproduction of Speech and Music.* By N. W. McLACHLAN, D.Sc., M.I.E.E., F.Inst.P., and G. A. V. SOWTER, B.Sc., A.M.I.E.E.*.

[Plate XV.]

SYNOPSIS.

1. Conical Diaphragm with Free Edge.
2. Conical Diaphragm with Reinforced Edge.
3. Conical Diaphragm with Rubber Surround.
4. Comparison of the Three preceding Cases.
5. Modes of Diaphragm corresponding to Upper Frequency Resonances.
6. The Upper Frequency Resonances—Influence of Coil Mass.
7. Resonances of the Moving Coils and their Formers.
8. Influence of Radius of Cone on Main or Second Centre Moving Symmetrical Mode.
9. Influence of ψ the Apical Angle of a Free-edge Cone on Frequency of Main Symmetrical Mode.
10. Influence of Thickness of Paper on Frequency of Main Symmetrical Mode.
11. Stresses in a Conical Sheet.
12. Experiments with Sheet Metal Cones.
13. Measurement of apparent Radiation Resistance R_m .
14. Method of detecting Miscoounted or Short-circuited Turns on a Coil.
15. Apparent Efficiency η_a .
16. Conclusion.
17. Appendix.

ABSTRACT.

THIS paper deals with the mechanical and acoustical behaviour of coil-driven conical diaphragms under various conditions. Three edge conditions are treated:—(a) free; (b) reinforced; (c) suspension by rubber surround. Case (a) is characterized by numerous radial modes at low frequencies, case (b) by an absence of these modes and a relatively weak lower register, and case (c) by augmentation of the lower register to the level of the upper register. The latter effect is due to the rubber surround acting as an auxiliary resonant diaphragm. The influence of the edge condition on the upper register is aurally unimportant for the standard size of diaphragm used in the experiments. The first centre moving symmetrical mode of a diaphragm 12 cm. radius and apical angle 90° occurs about 900 cycles, and the second and most powerful centre moving symmetrical mode about 2000 cycles. The frequencies of these modes decrease with increase in the apical angle from 90° towards 180° . For a 90° cone they are not seriously affected by

* Communicated by the Authors.

variation in the mass of the coil or the thickness of the paper. This points to radial expansion and contraction of circular sections of the cone as a whole, which is concomitant with circumferential tensile and compressive stresses. It is shown that the upper register increases in strength and in range with decrease in the mass of the coil. Owing to transmission and radiation losses, the so-called nodes are actually positions of minimum amplitude.

Experiments have been conducted with aluminium cones 1 mil and 3 mils thick. Although the main resonance was elevated appreciably the reproduction lacked body.

Difficulties encountered in ascertaining the sound output accurately from resistance measurements of the coil fixed and free are discussed in detail. The question of apparent efficiency is treated. The performance criterion is the total sound output at all frequencies in the acoustic register, and not merely a curve of axial air pressure.

An Appendix is given containing tables of resonance frequencies of different diaphragms, also the static resistance and inductance of 40 and 1000 turn coils situated in and out of the electromagnet. An approximate method of measuring the Accession to Inertia when the diaphragm does not move as a whole is outlined.

1. Conical Diaphragm with Free Edge.

A FREE-EDGE conical diaphragm having the dimensions given in Table I. is supported by four elastic threads, as shown in fig. 1 *b*.

TABLE I.

Showing Dimensions of Free-edge Conical Diaphragm.

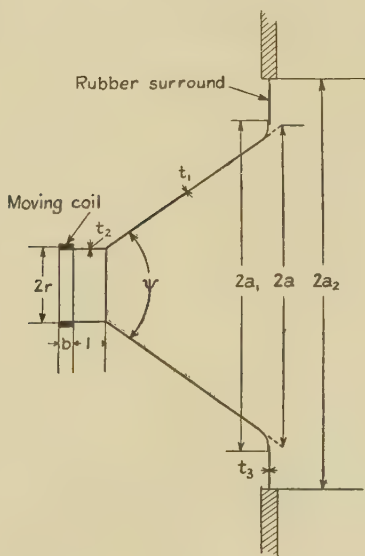
$a=12$ cm.
$l=2.5$ cm.
$t_1=2.1 \times 10^{-2}$ cm.
$t_2=2.1 \times 10^{-2}$ cm.
$n=1000$ turns.
$\psi=90^\circ$.
$M_c=7.84$ gm.
$H=7000$ lines cm. ⁻² approx.

No centering device was used for the coil, thereby avoiding resonance in the bass register due to oscillation of the

diaphragm as a whole. Such a condition would have introduced unnecessary complications.

In the absence of the magnetic field, the natural frequency of the diaphragm moving as a whole on the threads is less than three cycles per second. The moving coil was wound on a paper tube about 2×10^{-2} cm. thick. After the application of bakelite varnish the coil was baked in an oven at 110°C . for three hours. The paper tube was fixed to the diaphragm by serrating the end remote from the coil, bending it over and applying seccotine. In some experiments 1000

Fig. 1 a.



a = radius of free edge cone.

a_1 = " " reinforced edge cone.

a_2 = " " rubber surround.

r = mean radius of moving coil = 2.5 cm. throughout.

b = axial length of " " = 0.95 cm. "

l = free " " " " " former.

t_1 = thickness of conical sheet.

t_2 = " " coil former.

t_3 = " " rubber surround.

n = number of turns on coil.

ψ = apical angle of cone (plane).

M_c = mass of coil and former.

Air-gap = 0.32 cm. throughout, except table 15, where it is 0.24 cm.

H = Mean radial magnetic field $\doteq 7 \times 10^3$ lines cm.⁻², except table 15, where it is 1.1×10^4 lines cm.⁻².

774 Dr. N. W. McLachlan and Mr. G. A. V. Sowter on the turns were used, whilst in others 20 or 40 turns served the purpose.

The investigation of diaphragm performance was conducted mainly by bridge measurements of resistance and inductance with the coil free and with it fixed. The arrangements were identical with those described in an earlier paper * devoted to the measurement of Accession to Inertia. Customary precautions regarding screened leads, screened and balanced transformers, were taken, and it was always possible to obtain the readings, whether by vibration galvanometer or by telephone, to a high degree of accuracy. Assistance in this direction was given by a screened valve-amplifier between the bridge and the telephones. Three sets of the latter were used, having resonance frequencies at 500, 1000, and 2500

Fig. 1 b.

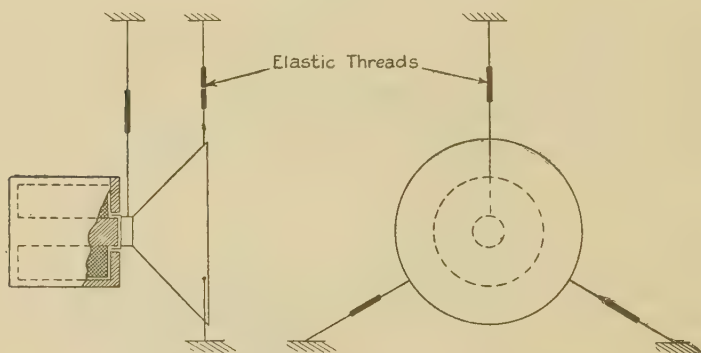


Diagram showing method of suspending the diaphragm by elastic threads. The baffle has been omitted.

cycles. The vibration galvanometer covered the range from 300 cycles downwards.

Starting about 45 cycles per second, a series of measurements of the following quantities was made :—

- L_0 = inductance with coil fixed.
- L_1 = " " " free.
- R_0 = resistance " " fixed.
- R_1 = " " " free.

So far as resonances are concerned, the behaviour of the diaphragm can be visualised by inspection of the variations

* Phil. Mag. xi. pp. 1137-52 (June 1931).

in the value of $(R_1 - R_0) = R_m$, the apparent radiation resistance (see section 13).

During vibration in a "radial mode," contiguous sectors of a homogeneous diaphragm move simultaneously in opposite directions. Moreover, considerable variations in the effective mass of the system—referred to the driving mechanism—are not to be expected. There is a slight variation due to asymmetry arising from the seam. The effect is to cause a slight rise and fall in L_1 over a narrow frequency band, introducing a maximum, a minimum, and a point of inflexion. As we shall see later, the variation in $L_m = (L_1 - L_0)$ and, therefore, in the effective mass, at a powerful symmetrical mode is appreciable. Consequently, it is sometimes feasible to discriminate between symmetrical and radial modes by inspection of the curve of motional inductance.

Since the variation in L_m at radial modes is so small, it is necessary to rely upon the apparent output resistance R_m as a criterion of diaphragm performance at low frequencies.

The quantity R_m can be regarded as the apparent acoustic radiation or output resistance. It includes diaphragm loss and variations in iron resistance, which are discussed in Section 13. This, however, is immaterial, since we are solely concerned in investigating the physical behaviour of the diaphragm, and not in an accurate determination of the acoustic energy output.

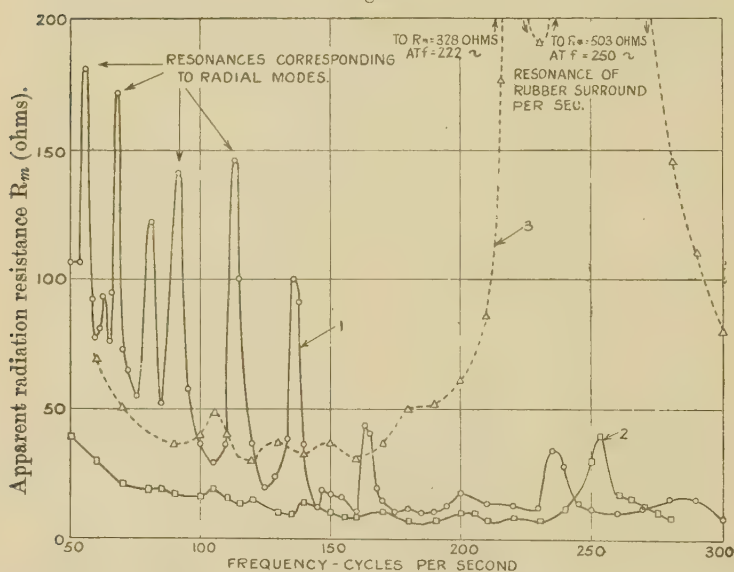
We saw previously * that a free-edge diaphragm exhibits radial modes at low frequencies. As a guide to the bridge measurements, it is useful to make a preliminary stroboscopic examination of the diaphragm to locate the low-frequency resonances. These resonances are comparatively sharp, and can easily be missed unless small frequency intervals are taken. A representative curve (No. 1) is plotted in fig. 2, which shows a number of sharply defined resonances. To locate these accurately, readings had to be taken to 0.1 cycle per second or even less, since the resonance lasted only a few cycles—about 6. There are a number of sharp peaks, each corresponding to a *radial* mode, starting about 50 cycles and continuing to 135 cycles, after which frequency their magnitude abates rapidly.

Above 250 cycles the radial modes are comparatively innocuous. In the tests described previously, irregularities in the frequency sequence of the modes was found, due to asymmetry arising from the extra mass and stiffness of the seam. Curve 1 of fig. 2 shows definite irregularities of the same nature as those obtained with a diaphragm of identical

* Phil. Mag. xi. p. 18 (Jan. 1931).

dimensions made from thinner paper *. The resonance frequencies from fig. 2 were plotted and a mean curve drawn through them. The values so obtained are taken to represent those for a symmetrical cone without a seam. The ratios† to the fundamental frequency are given in column 3, Table II., and by way of comparison the data from the previous paper are repeated in column 4. The agreement between the ratios for different thicknesses of paper is quite close. In the case of a flat disk, the fundamental frequency depends directly upon the thickness of the paper.

Fig. 2.



Apparent radiation resistance R_m corresponding to lower register of diaphragm with (1) free edge showing resonances due to radial modes; (2) reinforced edge showing suppression of radial modes; (3) rubber surround showing effect of the latter acting as an auxiliary resonant diaphragm.

With the cone the ratio of the paper thicknesses is $2.1 \times 10^{-2} / 1.4 \times 10^{-2} = 1.5$, whilst the ratio of the basic frequencies is $55/37 = 1.49$. It appears, therefore, that, *inasmuch as radial modes* are concerned, the basic frequency of a 90° cone depends directly upon the thickness of the material. This

* Phil. Mag. xi. p. 18 (1931).

† These are in great contrast with those for a flat disk, the ratios for the latter being much greater.

TABLE II.

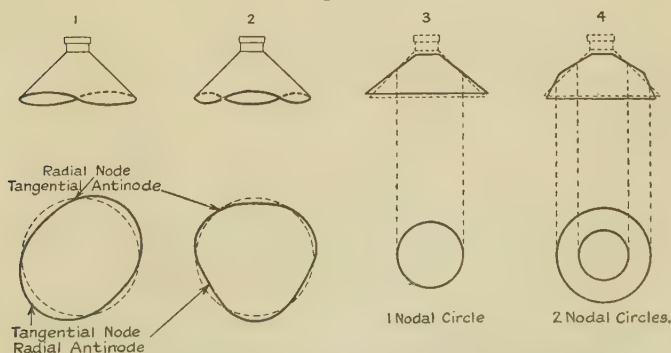
Showing frequencies of Radial Modes of a Free-edge Cone driven by a Circular Coil.

$a=12$ cm. ; $l=2.5$ cm. ; $t_2=2.1 \times 10^{-2}$ cm. ; $n=1000$ turns ;
 $\psi=90^\circ$; $M_c=4.7$ gm.

Frequency (cycles per second).	Number of Radial Nodes (from curve).	Frequency Ratio to Fundamental.	
		$t_1=2.1 \times 10^{-2}$ cm.	$t_1=1.4 \times 10^{-2}$ cm.
55	4	1.0	1.0 *
76	6	1.38	1.35
101	8	1.84	1.86
133	10	2.42	2.48
170	12	3.1	3.24
220	14	4.0	4.06
285	16	5.2	5.13
332	18	6.05	6.22

* This corresponds to a frequency of 37 cycles per second. See Phil. Mag. xi. p. 18 (Jan. 1931).

Fig. 3.



Diagrams showing shape of homogeneous isotropic lossless conical diaphragm when executing certain modes of vibration *in vacuo*. (1) First radial mode; (2) second radial mode; (3) first centre moving symmetrical mode; (4) second centre moving symmetrical mode. The sketches are purely diagrammatic.

frequency is, of course, much higher than it would be for a disk of equal thickness, but the subject will be discussed in a later paper.

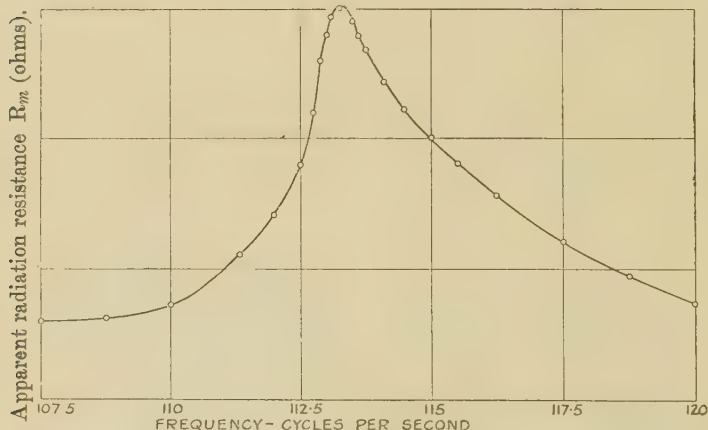
For the sake of completeness, fig. 3 has been included,

showing the shape of the diaphragm when executing certain modes, whilst fig. 4 is an enlarged view of a portion of fig. 2, corresponding to a radial mode at 113.3 cycles per second.

Above 250 cycles there are a succession of lesser resonances until at 800 to 950 cycles they become more prominent. Thereafter R_m decreases, but between 1700 and 3000 cycles there is another series of prominent resonances. These are displayed clearly in fig. 5, curve 2. It will be shown later that these sets of resonances are associated with the first and second centre moving symmetrical modes of the diaphragm respectively.

In this paper and elsewhere, the term "node" has been used quite freely. The condition of complete rest however,

Fig. 4.



Enlargement of radial mode of free-edge diaphragm at 113.3 cycles per second taken from fig. 2, curve 1. The vertical scale is the same as that of fig. 3.

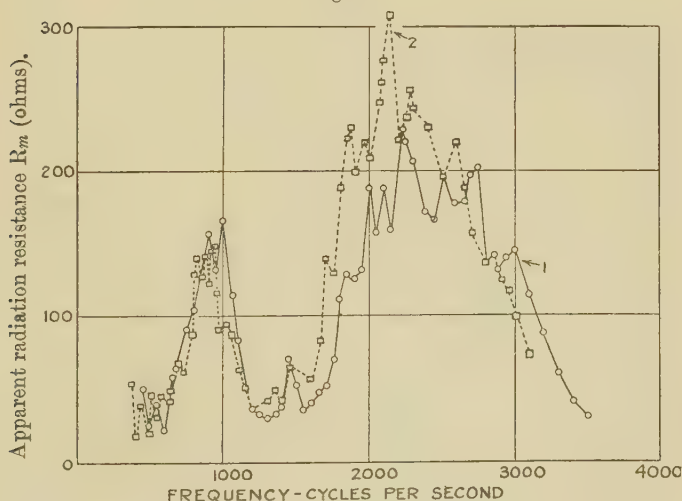
applies only to an ideal lossless structure vibrating *in vacuo*. With a centrally driven disk the energy transmitted from the centre is equal to that reflected from the periphery. At the first centre stationary mode these energies are equal in magnitude but opposite in phase. Thus a true node occurs. But in practice, owing to transmission and radiation loss, the reflected energy is less than and is not exactly in phase opposition to the transmitted energy. Consequently the centre is not an actual node, but merely a position of minimum amplitude. The greater the loss the greater is the amplitude at the centre. This argument applies equally to

other modes of vibration. Moreover, if the vibration is vigorous and the loss large, the positions of minimum amplitude are difficult to detect by aid of sand or powder. This aspect of the problem is treated in detail in a letter to 'The Wireless Engineer and Experimental Wireless,' Oct. 1931. Throughout the paper it is intended that the expression "nodal circle" should be interpreted in the above sense.

2. Conical Diaphragm with Reinforced Edge.

When the edge of the cone is bent over as shown in fig. 1, and reinforced by a ring of presspahn 0.7 cm. wide and

Fig. 5.



Apparant radiation resistance corresponding to upper register of diaphragm with (1) reinforced edge, (2) free edge.

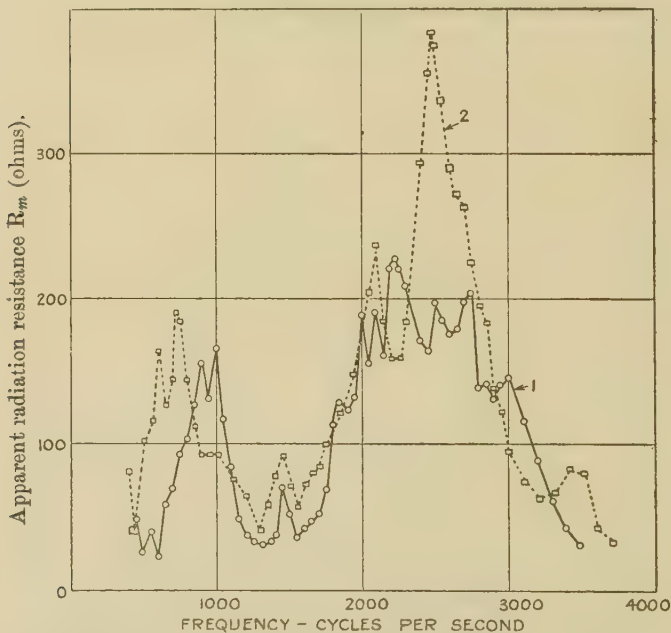
3.2×10^{-2} cm. thick, it is no longer able to bend as in the "free" state. Thus, the radial modes are not displayed as described in the previous section. The result of a series of measurements of R_m at low frequencies is shown in curve 2 of fig. 2. Not only have the radial modes been eliminated, but the apparent radiation resistance is a fraction of its former value. A slight resonance occurs at 250 cycles per second. Viewed stroboscopically it was seen to be caused by the seam of the cone. As pointed out in a former paper*,

* Phil. Mag. xi. p. 1148 (June 1931).

additional masses can cause the diaphragm to break up locally. Moreover, the seam was relatively at rest, whilst the portions of the diaphragm on either side moved in opposition.

Below 250 cycles there are small variations in R_m , but, as no break up effect was revealed by stroboscopic examination, these can be ascribed to variation in iron loss, *i. e.*, this loss differed for R_0 and R_1 , $(R_1 - R_0) = R_m$. The smoothness of the inductance curve of the diaphragm in motion supports this

Fig. 6.



Apparent radiation resistance corresponding to upper register of diaphragm with (1) reinforced edge, (2) rubber surround.*

view. Naturally, owing to the seam effect at 250 cycles a variation in L_1 occurred at this frequency.

Referring to fig. 5, curve 1, we see that the effect of the reinforced edge upon the upper register is comparatively small. The first centre moving symmetrical mode occurs from 900 to 1000 cycles as against 800 to 950 cycles for the free edge. The second centre moving symmetrical mode is 100 cycles higher than before, and there is a slight reduction in output over the band 1700 to 2800 cycles.

Since it is impossible to conduct tests on the same diaphragm with free and reinforced edges simultaneously, secular variations may have occurred during the interval. The moving coil had to be changed, since that used for the free-edge tests developed short-circuited turns. This might easily be accompanied by different conditions due to addition of seccotine or alteration in coil mass. However, owing to the insensitivity of the human ear, the upper register would sound identical with a free and with a reinforced edge.

3. *Conical Diaphragm with Rubber Surround.*

The condition in this case is the same as that which occurs in practical reproducers, excepting so far as the material of the annular support is concerned. In our experiments we used thin rubber sheet, whereas in practice it is customary to use leather. The rubber was secured to a square piece of thick cardboard held in a frame, having a hole 14 cm. radius. Apart from the bent-over portion of the diaphragm, to which the rubber was glued, the free portion of the annulus was 1.8 cm. wide.

Here again the bent-over edge, combined with the stiffening effect of glue and rubber, gives a reinforced condition which eliminates radial modes. Measurements on the same diaphragm as that used in the two previous sections are plotted in curve 3, fig. 2. An enormous increase in output occurs over the range 200 to 300 cycles, due to the influence of the rubber surround. The effect is that of an auxiliary resonant diaphragm*. Below 200 cycles the output is much greater than that with a reinforced edge alone. Unfortunately, this is not a good example of the influence of a rubber surround. So far as the reproduction of speech and music is concerned, the band of frequencies seriously influenced by the surround is much too narrow, owing to excessive radial tension. Moreover, fig. 7 has been reproduced to demonstrate that with a reduction in radial tension not only is the output level greater, but a wider frequency range is covered.

The resonance frequency f_1 of the surround *per se*—the diaphragm resonated on the surround at 18.7 cycles (f_0)—occurs at 129.5 cycles per second. Owing to asymmetry of the radial tension there is more than one peak. The main peak appears to be extremely large, but from an acoustic view-point it is not so serious as the diagram suggests. The ratio of the output at 129.5 cycles to that on the flat portion

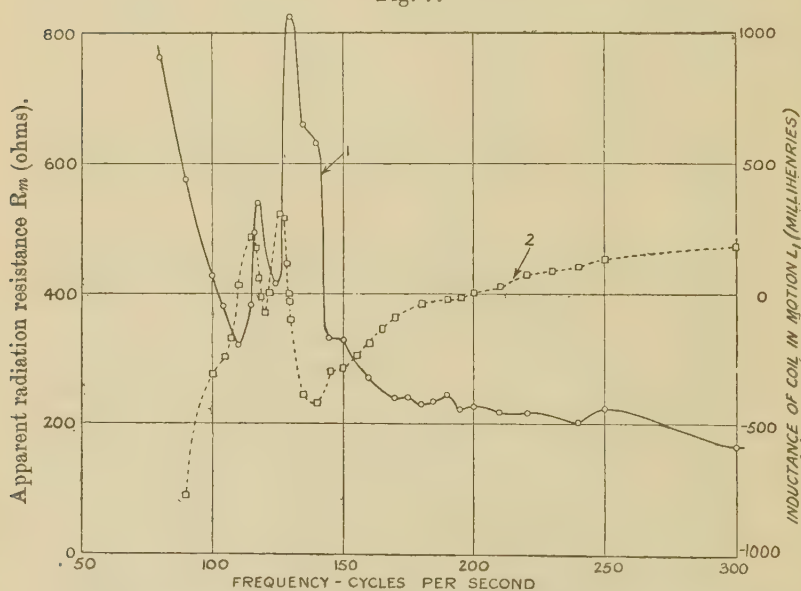
* Phil. Mag. xi. pp. 28-29 (Jan. 1931).

of the curve above 150 cycles is approximately 4/1. In sensation units this works out at 6 decibels, which is not really important at 129.5 cycles, owing to the lack of sensitivity of the ear to low frequencies.

We have already shown that the ratio $f_1/f_0 = \pi(m/m_1)^{1/2}$. In the above case it is $\frac{129.5}{18.7} = 7/1$, and this is in reasonable agreement with the value calculated from the formula.

Reference to fig. 6, curve 2, indicates that the main resonance in the 900-cycle region has travelled down to

Fig. 7.



- (1) Apparent radiation resistance corresponding to lower register of standard-size diaphragm with rubber surround and reduced radial tension. The resonance of the surround occurs at 129.5 cycles per second. Turns on moving coil=1200.
- (2) L_1 =inductance of coil in motion for diaphragm of curve 1. Owing to resonance of the surround there are five frequencies at which $L_1=0$. The electro-mechanical resonance of the system, apart from the elastic effect of the surround, occurs about 200 cycles per second.

700 cycles, due probably to the rubber. In fig. 9, which shows the complete register of a diaphragm (that of fig. 7) with rubber surround, a series of resonances will be seen from 700 to 1000 cycles.

4. Comparison of the Three preceding Cases.

We are now in a position to compare the three cases: (a) free edge, (b) reinforced edge, (c) supported edge. From an inspection of the curves one can see that the reinforced edge will give reproduction with a highly attenuated lower register. Obviously, this is of no value in commercial apparatus. The free edge appears to have a fairly good lower register. This is to an extent deceptive, since the musical register is not continuous but consists of a series of notes at definite frequency intervals. Some of these notes fall in the valleys of the curve, and on broadcast reproduction the bass register is not so powerful as one might expect. In the reproduction of percussion instruments like the piano the bass is weak, since the radial modes are rendered aperiodic by the damping of the magnetic field.

The bass register is fully restored in the case of the rubber surround, provided the natural frequency is not too high. A value below 129.5 cycles would doubtless be better, but the reproduction from this diaphragm is very pleasant indeed. With the surround frequency at 250 cycles the bass register appears to be good in certain cases, but is quite lacking in others. Also, there is a boom with speech.

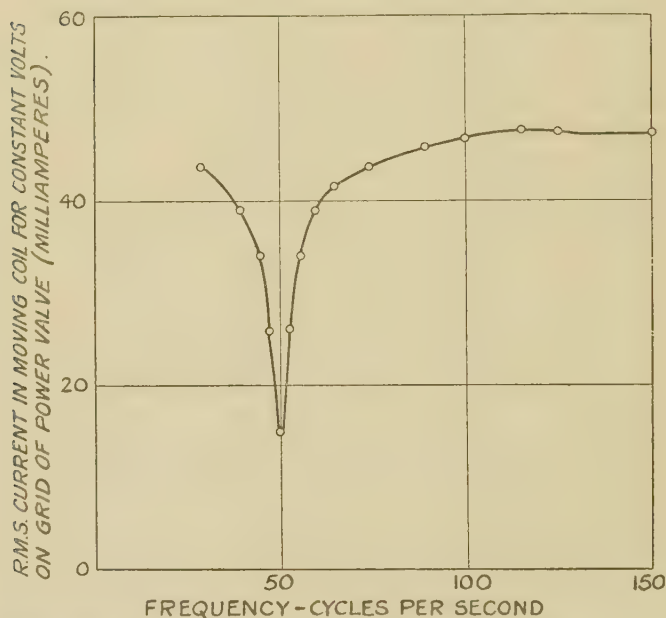
It will be shown in a later paper that the 129.5-cycle resonance is rendered aperiodic by the magnetic field, whilst the 250-cycle resonance is oscillatory. Moreover, the surround resonance should not occur above a certain frequency.

In some practical reproducers where the diaphragm resonates on a surround (other than rubber—*e. g.*, leather) or on a centering device between 50 and 100 cycles, there appears to be a powerful lower register. This, however, is located round the resonance frequency, and is decidedly objectionable. With a coil of 1000 turns the value of R_m , the actual radiation resistance corresponding to this resonance, is thousands of ohms, and where low resistance triodes are used a large reduction in the operating alternating current occurs. To illustrate this point concretely, fig. 8 has been reproduced. Obviously, since the sound output depends upon $I^2 R_m$, the reduction in current mitigates the resonance a good deal. In the example shown, the current at resonance is one-third its normal value, thereby reducing the output to one-ninth the value which would obtain in a constant-current system—*e. g.*, a pentode. With the latter valve, resonances of this nature are positively terrible.

An approximate calculation shows that the radiation resistance of the diaphragm at the resonance frequency is

of the order 5000 ohms, or nearly four times the effective resistance of the coil when fixed. This gives an efficiency—apart from the valve—approaching 80 per cent. With a triode having $\rho=3000$ ohms the output at 50 cycles would be about four times that at 100 cycles, whereas with a pentode having $\rho=30,000$, the output ratio would be about twenty. These data clearly demonstrate the influence of valve resistance upon the output at resonance.

Fig. 8.



Curve showing a.c. through moving coil having 1000 turns when diaphragm resonates as a whole on a surround at 50 cycles per second. The voltage applied to the grid of the valve was constant at all frequencies. The radiation resistance of the system at 50 cycles is some 25 times its normal value, corresponding to an efficiency of nearly 80 per cent.—the valve is not included in this estimate.

Comparison of the upper register presents no difficulty, since the aural difference between the three cases is insignificant. Tables III. and IV. have been included to show more clearly the relationship of the three cases for the same diaphragm at resonant and at non-resonant frequencies. With a rubber surround or with a free edge, the upper register in the neighbourhood of 2500 cycles exceeds

TABLE III.

Showing Comparison of Output from Coil-driven Conical Diaphragm, with (a) Free Edge, (b) Reinforced Edge, (c) Rubber Surround, at Resonant Frequencies.

$a=12$ cm.; $a_1=12.2$ cm.; $a_2=14$ cm.; $l=2.5$ cm.;
 $t_1=t_2=2.1 \times 10^{-2}$ cm.; $t_3=1.6 \times 10^{-2}$ cm.; $n=1000$
 turns; $\psi=90^\circ$; $M_c=4.7$ gm.

Condition (a).		Condition (b).		Condition (c).	
Frequency (cycles per second).	Free edge, R_m (ohms).	Frequency (cycles per second).	Reinforced edge, R_m (ohms).	Frequency (cycles per second).	Rubber surround, R_m (ohms).
54.8	183				
62.6	94				
68	173	72	28		
81	122				
92.6	141	92.5	23		
113.5	146			105	
136	101			150	
164	43	181	8.5	170	
235	34			222	
285	18	290	32	250	
332	40			324	
375	52	350	108		
420	37				
495	45	450	50		
575	45	550	40	590	
680	66			740	
810	141	First cr. stationary mode at intermediate freq.			
875	139	900	156		
915	147	1000	166		
1350	49				
1450	65	1450 *	71	1450 *	92
1700	140			1750	101
1860	232	1850	128		Begins to rise here.
1960	221	2000	188		
2125	309	2100	190	2100	239
2275	258	2225	228		
2600	220	2500	198	2490	384
2850	142	2750	203	3400	84

Not actually resonances.

Minor effect.

Resonance of
surround per sec.

900-cycle resonance
lowered due to rubber.

First centre moving
symmetrical mode.

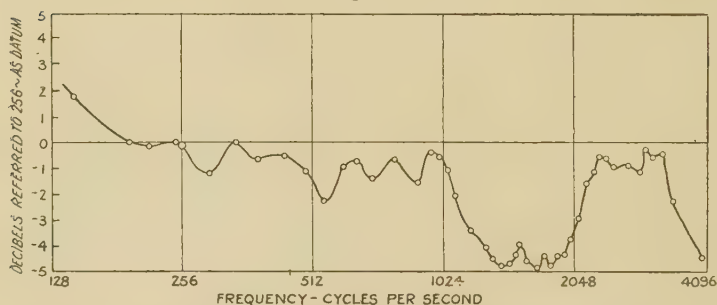
Second centre moving
symmetrical mode.

* Neighbourhood of second centre stationary mode. The sequence first centre stationary, first centre moving, etc., should be noted.

that of the reinforced edge. The complete curve for the diaphragm of fig. 7 has been reproduced in fig. 9 on a decibel basis. Here we see a definite dip between 1000 and 2000 cycles, which is a characteristic of the diaphragm caused by the main centre moving symmetrical resonances being located in the 1000- and 2500-cycle regions. The output decays above 3500 cycles, due to transmission loss and interference, but this applies equally to the other edge conditions.

The effective mass curves for conditions (b) and (c) in Table III. are given in 'The Wireless World and Radio Review,' Aug. 12th, 1931. M_e is calculated from the expression $M_e = -[C^2/\omega^2 L_m][z^2/(1+z^2)]$, where $L_m = (L_1 - L_0)$, $R_m = (R_1 - R_0)$, and $z = \omega L_m/R_m$. When $z^2/(1+z^2)$ is substantially unity, $M_e = -C^2/\omega^2 L_m$ which is identical with the

Fig. 9.



Output curve of diaphragm cited in fig. 7, the ordinates being decibels, and the datum 256 cycles per second (middle C on pianoforte).

expression used to find the accession to inertia of a rigid diaphragm*.

5. Modes of Diaphragm corresponding to Upper Frequency Resonances.

We have already seen that radial modes occur at low frequencies when the edge of the diaphragm is free to bend. Also, that reinforcement of the edge suppresses these modes, although above 200 cycles they probably exist to an extent between the edge and the apex. It has been suggested that the first centre moving symmetrical mode of a diaphragm

* Phil. Mag., June 1931. These formulæ can be deduced from expressions (5), (11), (12) and that on p. 1033, Phil. Mag. vii., and pp. 1015-17, Suppl., June 1929, by putting $M_e = m$ and $L_m = (L_1 - L_0) - \frac{1}{2}wC_m$. B is the total mechanical resistance due to losses and sound radiation.

with $a=12$ cm., $\psi=90^\circ$ occurs between 800 and 1000 cycles, and the second symmetrical mode between 1700 and 2300 cycles. The frequency of the latter mode depends to an extent upon the rigidity of the coil connexion to the diaphragm; with appreciable reinforcement the frequency increases. The short coil neck (free former length) would increase the rigidity and raise the frequency as in fig. 9.

TABLE IV.

Showing Comparison of Output from Coil-driven Conical Diaphragm, with (a) Free Edge, (b) Reinforced Edge, (c) Rubber Surround, at Non-Resonant Frequencies.

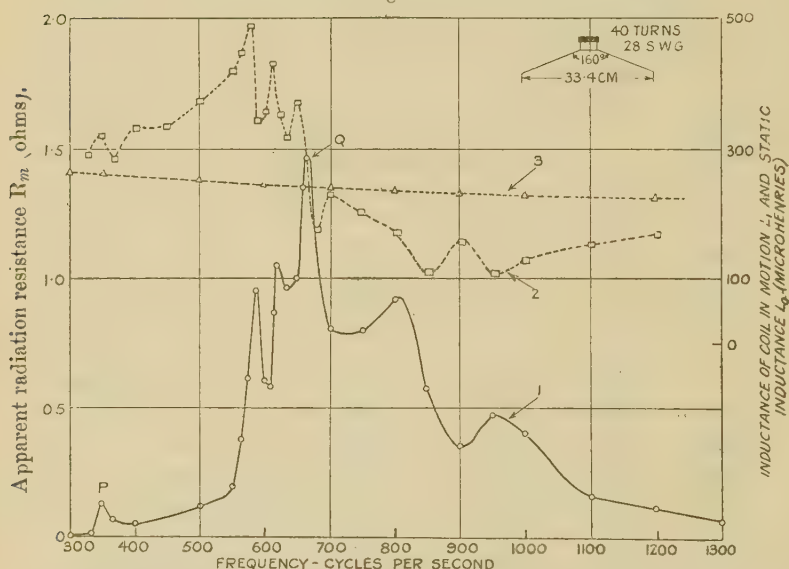
Conditions as for Table III.

Frequency cycles per second).	R_m (ohms).		
	Free edge.	Reinforced edge.	Rubber surround.
100	36	10	39
120	37	7	30
160	10	4	30
180	12	8	50
270	11	7	235 near resonance.
400	17	16	80
600	43	22	133
1200	36	37	64
1600	55	41	72
3000	97	144	91

To view the diaphragm stroboscopically at these frequencies, optical magnification would be required, since the amplitude of the vibration is so small. The use of lycopodium powder is precluded, since it will not stay on the diaphragm during vibration and merely slides off the surface owing to the steepness of the sides of the cone. To overcome this difficulty, a large flat cone of thick paper, having the dimensions shown in fig. 10, was constructed. When this was flexibly suspended with the concave side upwards, dust figures could be obtained, provided the amplitude of vibration at the so-called nodal positions was not too large to make the powder roll to the apex.

The resonance frequencies were located by bridge measurement. A sine wave current was supplied to the moving coil at these frequencies, the corresponding nodal patterns being observed. The surface was explored by aid of a button microphone mounted on a thick wire feeler and connected *via* a battery to a pair of telephones. The result of the bridge measurements is shown in fig. 10, the output resistance being plotted in curve 1. A small resonance occurs at 350 cycles, this being accompanied by a nodal circle and numerous radial

Fig. 10.



- (1) Apparent radiation resistance R_m for large flat cone ($\alpha=16.7^\circ$, $\psi=160^\circ$), showing the first symmetrical mode at P=350 cycles and the second symmetrical mode at Q=664 cycles per second.
- (2) L_1 =inductance of coil in motion for diaphragm of curve 1. Variations in inductance correspond to changes in the effective mass of the dynamical system. This curve cuts the static inductance curve at $f=664$ cycles, showing that the effective mass is zero at the second centre moving symmetrical mode. See Section 4 for formula relating to M_e .
- (3) L_0 =inductance of coil when fixed (see Table XIX. for values).

nodes. The main or major resonance occurs at 664 cycles. It is accompanied by two nodal circles and radial nodes. There are two other resonances at 590 and 620 cycles, probably due to asymmetry caused by the seam and the

heterogeneous nature of the paper. A similar effect is obtained with other classes of paper. The resonance at 950 cycles is accompanied by three nodal circles and radial nodes.

Although the term circular nodes has been used, it merely signifies the form of the figure with a symmetric homogeneous conical sheet. The actual dust figures were quite irregular and not always continuous. This is clearly due to asymmetry and heterogeneity of the paper. The amplitude of the diaphragm a short distance from the coil exceeded that of the latter. At certain frequencies an annulus midway between the coil and the periphery moved relatively little.

The inductance of the coil in motion is plotted in fig. 10, curve 2. The variations in this case are an excellent guide to the behaviour of the diaphragm. The points of inflexion in the curve occur approximately at the corresponding resonance frequencies. Curve 2 crosses the static inductance curve 3 at the resonance frequency of 664 cycles, which indicates that the dynamic condition contains no mass—*i. e.*, M_e the effective mass of the system is zero. Below 664 cycles per second $L_1 > L_0$ and M_e is negative, whilst above 664 cycles per second $L_0 > L_1$ and M_e is positive. M_e is also positive below 240 cycles per second, at which frequency the first centre stationary mode occurs—not shown in diagram.

A list of some of the modes is given in Table V.

TABLE V.

Showing Frequencies of various Modes of Free-edge
Coil-driven Conical Diaphragm.

$a = 16.7$ cm.; $l = 2.5$ cm.; $t_1 = 5 \times 10^{-2}$ cm.; $t_2 = 2.1 \times 10^{-2}$ cm.;

$n = 40$ turns 28 s.w.g. ; $\psi = 160^\circ$; $M_c = 7.84$ gm.

Total natural mass of diaphragm $M = 48$ gm.

Frequency (cycles per second).	Nodal pattern.	R_m . Apparent radiation resistance (ohms).
49.2	Four radii.	1.22
71	Six radii.	0.193
97	Eight radii.	0.142
Intermediate	Not observed.	Not observed.
350	One circle and radial nodes.	0.128
664	Two circles and radial nodes.	1.46
800	Not observed.	0.92
950	Three circles and radial nodes.	0.48

As usual, the radial nodes viewed stroboscopically were irregular, and the same pattern occurred at more than one frequency. The data in the table are taken from the bridge measurements.

Due to asymmetric motion, the radial modes at low frequencies were accompanied by considerable noise caused by bending of the stiff paper. This resembled a well-known stage effect used for simulating violent storms. By aid of a high-quality microphone the output from the diaphragm under these conditions was recorded, with the result portrayed in fig. 11 (Pl. XV.). On the low-frequency wave (49.2 cycles) a high-frequency ripple of large amplitude is superposed. The frequency* of the ripple is identical with that of the main centre moving symmetrical mode of the diaphragm. Evidently this radial mode was sufficiently energetic to impulse the diaphragm, causing it to radiate at its main centre moving symmetrical resonance frequency.

These experiments show that the main radial modes pertain to the lower frequencies, whilst the centre moving symmetrical modes occur at higher frequencies, the second mode being the most powerful. Moreover, we infer that the resonances of a 90° cone at 900 and 2000 cycles are the first and second centre moving symmetrical modes. These results are in striking contrast with those for a circular disk, where the first radial and centre moving symmetrical modes occur at approximately the same frequency. As will be seen later, the reason for this is to be sought in the different stresses in cone and disk. In the cone case there is circumferential tension (amongst others), whilst in a disk the stresses are entirely due to bending and shear.

6. *The Upper Frequency Resonances—Influence of Coil Mass.*

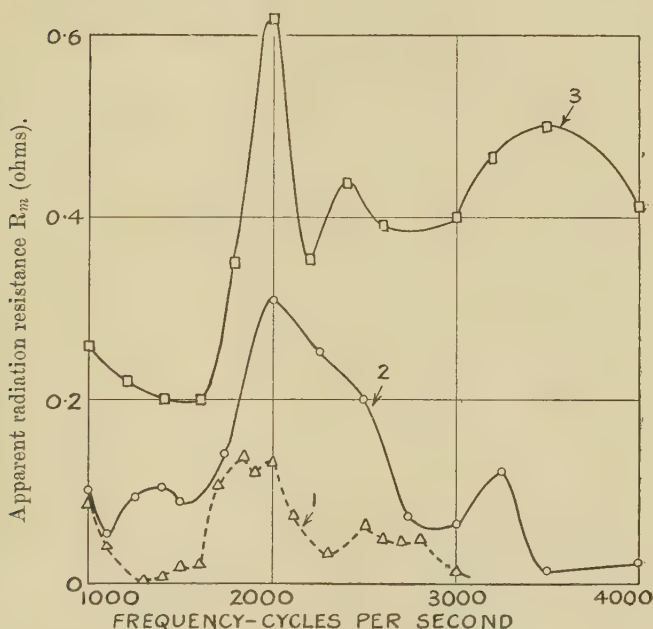
Having shown in previous sections how the lower register can be modified by the condition of the edge, we now proceed to show how the upper register can be varied by altering the mechanical properties of the moving coil. In fig. 12, three curves are plotted for the same diaphragm taken with different types of coil, particulars of which are given in Table VI.

Although the masses of the coils are very different, the frequency of the main symmetrical mode is not influenced

* An alteration had been made to the diaphragm since the curves of fig. 10 were taken, and the main resonance was higher than 664 cycles per second.

seriously, since it always occurs in the vicinity of 2000 cycles. Moreover, the diaphragm cannot be considered to act either

Fig. 12.



Apparent radiation resistance R_m of standard diaphragm driven by coils whose properties are given in Table VI.

TABLE VI.

Showing Particulars of Coils used for the Curves of Fig. 12.

$a_1 = 12.2$ cm.; $t_1 = 2.4 \times 10^{-2}$ cm.; $n = 40$ turns;
 $\psi = 90^\circ$; Reinforced Edge.

Item.	Curve 1.	Curve 2.	Curve 3.
Mass of coil (gm.).....	12.0	{ 6.84 1.0 }	1.8
Mass of former (gm.)			
Wire of coil (s.w.g.)	42 d.w.s.	28 d.w.s.	42 d.w.s.
Thickness of former, t_2 (cm.)	1.3×10^{-1}	2.1×10^{-2}	2.1×10^{-2}
Length of coil b (cm.)	0.95	0.95	0.95
Free length of former l (cm.)	2.5	2.5	2.5

as a disk or a simple coil spring, where added mass would lower the frequency. The action is to be sought in the nature of the stresses, which are partly circumferential.

Curve 1 for a paxolin tube-former of mass 12 gm. shows a comparatively low output, although the register above 2000 cycles is fairly well maintained*. This was confirmed by tests on broadcast reproduction.

Curve 2 for a 28 s.w.g. coil on a paper tube (total mass 7.84 gm.) shows a greater output than with the paxolin, whilst the 2000-cycle resonance is slightly more prominent.

Curve 3 is for a very light coil and shows a large increase in output, particularly above 2000 cycles. On broadcast reception the combination of the diaphragm with this coil was distinguished by a good upper register. In cases of this nature where the resonance is not characterized by a single well-defined peak, also where multiple resonance occurs, any doubts concerning the frequency of the main mode can be dispelled by taking an impulse test†. In fig. 9 resonance occurs above 2000 cycles. This is doubtless due to the shorter neck and greater rigidity of the coil condition than that in figs. 12, 13. Also the rubber surround probably augments the frequency (see Table III.).

A case of interest is exhibited in fig. 13. Curve 1 refers to a diaphragm actuated by a double layer coil of 40 turns 28 s.w.g., whilst curve 2 shows the effect of removing the upper layer. For direct comparison the ordinates of curve 2 should be quadrupled. The lighter coil shows a greater relative output, and the register above 2000 cycles has been extended. As before, the main resonance near 2000 cycles persists in both cases. It is clear that a reduction in coil mass for a given number of turns is accompanied by an increase in apparent radiation resistance, since, for a given current, the coil has a greater axial motion‡. What is not obvious, however, is the maintenance of the output at a high level from 2000 to 4000 cycles, curve 3, fig. 12. This coil and its former as a unit was much more flexible than either of those used for curves 1 and 2. Moreover, the large output above 2000 cycles may possibly be associated with the flexural modes of the coil combined with resonance tendencies of the diaphragm.

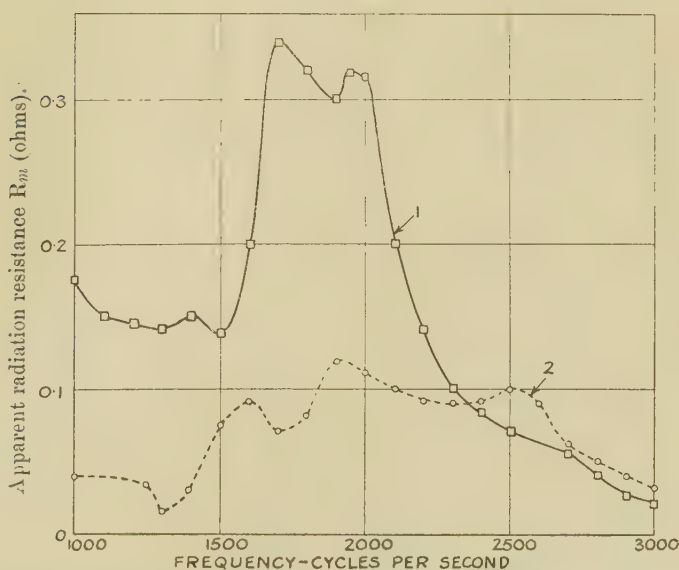
* In this case the first symmetrical mode at 900 cycles ($R_m=0.19$) was more powerful than the second at 1850 cycles ($R_m=0.14$).

† Phil. Mag. xi. p. 48, section 17 (1931).

‡ The effective mass of the diaphragm at 2000 cycles is quite a small proportion of the natural mass. (See 'Wireless World,' fig. 12, Aug. 12th, 1931.)

Experiments have been conducted with coils of equal mass and resistance, but different flexibility. Each coil had 40 turns of 42 s.w.g. wound on a paper former and bakelized. One was single layer, the other treble layer, so that its inductance was trebled. This caused a reduction in current at the upper frequencies, but, as explained below, it would not be serious. Tested on broadcast reception with an appropriate transformer, little difference in performance was discernible by ear. The upper register was good in both cases, but the overall output level suffered reduction

Fig. 13.



Apparent radiation resistance of standard free-edge diaphragm driven by (1) double-layer coil of 48 turns 28 s.w.g., (2) single-layer coil of 20 turns 28 s.w.g.

due to the d.c. resistance of each coil being 18 ohms, which is several times the customary value.

In work of this nature a good joint between the coil former and the cone is imperative. Preliminary tests were made on a cone with a central hole larger in diameter than the coil former. The latter was cut longitudinally at intervals of 1 cm. and the strips glued to the cone, thereby making a flexible joint. The upper register was very weak. By mounting the coils on new cones in the usual way, the upper

register was restored. If the cone is reinforced at the joint by a strip 2 cm. wide, the upper register is enhanced, since the stiff central portion moves as a whole at higher frequencies than before. In this respect care should be taken to make similar joints when comparing different coils.

The preceding tests are satisfactory from an aural view-point, but actual measurement is required to discriminate absolutely between the influence of mass and flexibility. If the mass influence predominates, a coil 1 cm. radius should have a better upper register than one 2 cm. radius, other things being equal. The general output level would be less owing to the smaller magnet causing a reduction in the force factor $C = 2\pi r n H$.

In interpreting curves of the type exhibited in fig. 12, it must be remembered that they apply only when the current is constant. Moreover, such curves are only indicative of the mechanical and acoustical properties of the diaphragm under this condition. Owing to inductive and capacitive reactance, the coil current is reduced at each end of the acoustic register, as shown previously*, unless the ohmic resistance is adequately high. Two 40-turn coils of 28 and 42 s.w.g. have equal inductances, but the resistance of the latter is 18 times that of the former. Using a perfect transformer, the resistance of the 42 s.w.g. swamps the coil reactance over a wide frequency band. This does not hold with 28 s.w.g. Thus, with 42 s.w.g. the current is substantially constant, but with 28 s.w.g. it increases in the middle register. Although the smaller wire entails a lighter coil and an increased amplitude, this is offset by a reduction in current. The general output level is reduced, but there is a relative gain in the upper register due to (a) constant current, (b) greater radiation resistance.

With a practical transformer this gain may not be so marked as curve 3, fig. 12, indicates, owing to leakage reactance†. Provided the sum of the leakage and coil reactances is small compared with the resistance, the gain is appreciable.

7. *Resonances of the Moving Coils and their Formers.*

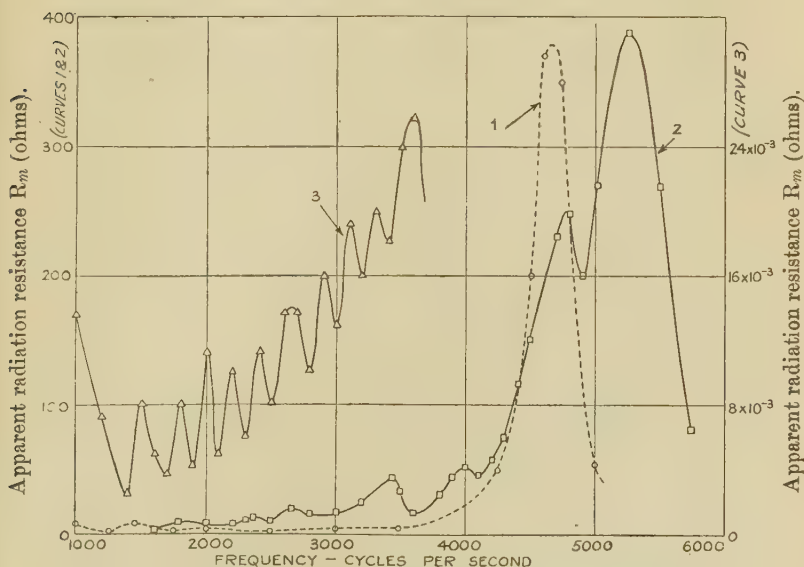
In an earlier paper we showed that coils exhibited flexural modes which could be excited by aid of a violin-bow. Here we have approached the problem from a different view-point. The end of the former remote from the coil was serrated, bent

* Phil. Mag. vii. p. 1032, figs. 6 & 7 (Suppl., June 1929).

† 'Wireless World and Radio Review,' March 30th, 1927.

over, and securely glued to a cylindrical lead block weighing 6 kilograms, whose lowest natural frequency was outside the audible limit. The electromagnet was placed with its axis vertical, and the block mounted so that the coil was in the radial magnetic field. A series of measurements was made of R_a at different frequencies, and these are exhibited graphically in fig. 14. Starting with curve 1 for a coil of 40 turns 28 s.w.g., up to 4000 cycles there is no resonance of any importance. Just above 4600 cycles there is an enormous peak, due to the longitudinal resonance of

Fig. 14.



Apparent radiation resistance of coils whose formers were securely fixed to a heavy lead block in place of a diaphragm.

- (1) 40 turns of 28 s.w.g. on paper tube to a vertical scale 500 times full size.
- (2) 1000 „ „ 47 enamelled on paper tube.
- (3) 40 „ „ 42 d.w.s. on paxolin tube:

See Table VI. for thickness.

the coil on the paper former. This frequency is in fair agreement with that calculated from known mechanical properties of the coil and the paper. ($E = 1.9 \times 10^{10}$ dynes cm^{-2} , $\rho = 0.67$ gm. cm^{-3} .)

Curve 2 represents the results for a coil of 1000 turns of 47 s.w.g. enamelled wire whose mass was about 4 gm. This

coil was more flexible than that cited above. There is now a greater tendency for resonances to occur, those at 3500 and 4000 cycles being quite large. The longitudinal resonance occurs at 5250 cycles and is of approximately the same magnitude as that obtained with the heavier coil on a shorter former—due allowance being made for the difference in the number of turns. In this case there is a preliminary resonance at 4750 cycles per second.

The snake-like appearance of curve 3 portrays the results with a thick paxolin former. To segregate the curves, this case has been plotted to a different scale.

Below 4000 cycles these curves must be interpreted with caution. From section 13 we see that the iron loss differs when the magnetic field is off and on, and one might be tempted to ascribe the variations in R_m to the iron. Above 1500 cycles the iron loss usually makes R_m less than its actual value. From 1500 to 4000 cycles the three curves differ appreciably. If the behaviour of the iron is the same in each case—the magnetization would be greatest for curve 2—the peaks appear to indicate resonances. These may be due to flexure of the coil and/or its former, unless the e.m. forces between adjacent layers are adequate to cause relative motion of the turns. The effect is greatest for the 1000 turn coil, this being the most flexible. Without further evidence curve 3 is inexplicable. If the coil takes up an oval shape—say, its first mode with 4 nodes—then, since the end secured to the lead block is immobile, there must be axial extension and contraction of the free end. When the coil and its former are secured to a diaphragm, the rigidity of the connexion is not comparable with that on the lead block. Moreover, flexure of the coil will be facilitated, so that greater resistance values would be forthcoming. On these grounds it is possible that, especially in curve 2, fig. 12, the flexibility of the coil—in addition to its reduced mass—assists the upper register.

The results of fig. 14 also show how futile it would be to simulate fixation of the coil by loading the diaphragm with sand or metal blocks. This matter is treated in detail in section 13.

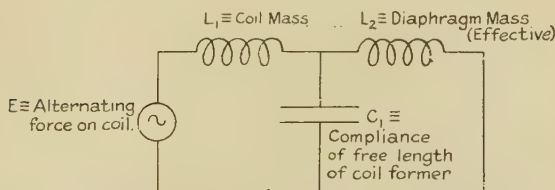
Knowing the frequency of the longitudinal resonance of the coil on its former, we can deduce that this mode does not figure in the reproduction of speech and music. With a former 2.5 cm. free length, the resonance occurs at 5250 cycles. In practice, the length would not exceed one-quarter this value, so that on a lead block the frequency would lie beyond 10,000 cycles. But the effective mass of a diaphragm

at frequencies of this order is very small*, so that the resonance must occur well beyond 10,000 cycles. This can be seen more clearly by inspection of fig. 15, which is the electrical analogue of the mechanical system. The mass of the coil is represented by L_1 †, the longitudinal compliance of the neck by C_1 , and the mass of the diaphragm by L_2 . The combined inductance of L_1 and L_2 in parallel is $\frac{L_1 L_2}{L_1 + L_2}$, which reduces to L_1 when L_2 is ∞ , *i. e.*, the lead-block condition, so that

$$f = \frac{1}{2\pi} \left(\frac{1}{L_1 C_1} \right)^{1/2} = 10^4 \text{ cycles.}$$

Assuming, by way of example, the mass of the coil to be four times that of the diaphragm at high frequencies, we get

Fig. 15.



Electrical analogue of mechanical system corresponding to coil and diaphragm. The cylindrical former between the two supplies the elastic member whose longitudinal compliance is equivalent to C_1 .

$L_2 = \infty$ for lead-block experiments.

the inductance of the combination as $L_1/5$ and $f'/f = (5)^{1/2}$, or $f' = 2.23 \times 10^4$ cycles per second, which is supersonic.

8. Influence of Radius of Cone on Main or Second Centre Moving Symmetrical Mode.

The diaphragms discussed hitherto have had a peripheral radius bordering on 12 cm., and for an apical angle of 90° the main or most powerful centre moving symmetrical mode occurs at a frequency of about 2000 cycles. The question arises, therefore, as to the influence of the radius of the cone upon this mode of vibration. One would expect a smaller cone to have a higher resonance frequency, and this is corroborated by

* See 'Wireless World,' fig. 11, Aug. 12th, 1931.

† This L_1 must not be confused with the inductance of the coil in motion.

experiment. The experiments in this direction have only been conducted with free-edge cones.

Data are collected in Table VII., showing the frequencies of the main symmetrical mode of a free-edge diaphragm whose radius was successively reduced.

TABLE VII.

Showing Frequency of Main or Second Centre Moving Symmetrical Mode of Free-edge Cones of different Radii.

$l = 2.5$ cm. ; $t_1 = t_2 = 2.1 \times 10^{-2}$ cm. ; $n = 40$ of 28 s.w.g. ;
 $\psi = 90^\circ$. ; $M_c = 7.84$ gm

<i>a.</i> Radius of cone (cm.).	<i>f.</i> Resonance frequency (cycles per second).
12	2000
7.8	2600
5.0	3500

TABLE VIII.

$l = 2.5$ cm. ; $t_1 = t_2 = 2.1 \times 10^{-2}$ cm. ; $n = 40$ turns 28 s.w.g. ;
 $\psi = 60^\circ$; $M_c = 7.84$ gm. ; Free Edge.

<i>a.</i> Radius of cone (cm.).	<i>f.</i> Main resonance frequency (cycles per second).	First symmetrical mode (cycles per second).
12	2200 ($R_m = 0.47$ ohm).	650 ($R_m = 0.32$ ohm).
8.5	2750 } multiple resonance.	1000
	3000 }	

Taking logarithms and plotting the data of Table VII. we obtain the relationship

$$f = 1.04 \times 10^4 a^{-0.671},$$

indicating that the frequency of the mode tends to approximate roughly to an inverse square-root law, which is in great contrast to a disk. Once again this points to fundamental differences in the mechanical stress conditions in disks and conical sheets. For an apical angle of 180° *i. e.* a disk,

the frequency of the second symmetrical mode, $f \propto a^{-2}$ and the index will therefore decrease with reduction in the apical angle.

Experiments were also performed using cones having apical angles of 60° and 135° , and the results are set forth in Tables VIII. and IX. respectively.

In both cases as the radius is decreased beyond a certain value, the resonance is a multiple one. The probable reason for this is discussed in section 11.

TABLE IX.

$l=2.5$ cm. ; $t_1=t_2=2.1 \times 10^{-2}$ cm. ; $n=40$ turns 28 s.w.g. ;
 $\psi=135$; $M_c=7.84$ gm. ; Free Edge.

<i>a.</i> Radius of cone (cm.).	<i>f.</i> Main resonance frequency (cycles per second).	R_m (ohm).
15.7	850 to 875	1.0
12	900	1.275
9.5	750	0.37
	900	0.43
	1000	0.52
	1100	0.73

9. *Influence of ψ , the Apical Angle of a Free-edge Cone upon the Frequency of the Main Centre Moving Symmetrical Mode.*

Starting with a paper disk 12 cm. radius, for which $\psi=180^\circ$, the first centre moving symmetrical mode will occur at a very low frequency. If the radius is constant, the cone becomes stiffer with decrease in apical angle and the frequency of the main symmetrical mode rises. A point is reached, however, when the increase in stiffness is substantially counterbalanced by increase in mass, and the frequency increases very slowly with reduction in the apical angle. This argument is exemplified by the data of Table X.

10. *Influence of Thickness of Paper on Frequency of Main Centre Moving Symmetrical Mode.*

The resonance frequency of a flat disk increases directly as its thickness, provided the radius is constant—i. e., the stiffness increases more rapidly than the mass. This is, of course,

TABLE X.

Showing Frequency of Main Centre Moving Symmetrical Mode of Free-edge Cones of Constant Radii and Variable Apical Angle.

$a=12$ cm. ; $l=2.5$ cm. ; $t_1=t_2=2.1 \times 10^{-2}$ cm. ;
 $n=40$ turns 28 s.w.g. ; $M_c=7.84$ gm. ; Free Edges

ψ . Apical angle (degrees).	f . Resonance frequency (cycles per second).	R_m (ohm).
60	2200	0.47
90	2000	0.3
135	900	1.275 (smaller losses in paper at lower frequency).
180	44 (without coil).	

TABLE XI.

Showing Influence of Paper Thickness on Frequency of Main Centre Moving Symmetrical Mode.

$a=12$ cm. ; $l=2.5$ cm. ; $t_2=2.1 \times 10^{-2}$ cm. ;
 $n=40$ turns of 28 s.w.g. ; $\psi=90^\circ$; $M_c=7.84$ gm.

t_1 . Thickness of paper (cm.).	f . Resonance frequency (cycles per second).	R_m (ohm).
1.52×10^{-2}	1800	0.32
2.14 "	2000	0.32
4.2 "	2100	0.52
4.2 "	2700	0.24
5 "	2400	0.5
5 "	2800	0.48

Same class of
paper.

Stiffer class of
paper, giving
higher $(E/\rho)^{1/2}$

consistent with a moment of resistance, having fourth-power dimensions as against third-power dimensions for a mass. In conical sheets where $\psi < 180^\circ$ the above does not hold, since bending becomes of less importance as ψ decreases. Table XI. has been compiled to show the influence of paper thickness upon the frequency of the main symmetrical mode.

From the first two rows of Table XI. we see that a 40 per cent. increase in thickness is accompanied by an elevation in frequency of only 16 per cent. From the second and third rows we see that doubling the thickness introduces two resonances at 2100 and 2700 cycles, but the former is more than twice as powerful as the latter. Thus, when $\psi = 90^\circ$ and $a = 12$ cm., the main mode is not seriously affected by the thickness of the paper. Variation in the thickness would be expected to have a marked effect when ψ approached 180° . Altering the paper to one of a stiffer class elevates the resonance as shown in the 5th and 6th rows of the table.

The same type of coil was used to obtain the data in sections 8, 9, and 10, namely, 40 turns 28 s.w.g. on a paper former 2.1×10^{-2} cm. thick, 2.5 cm. free length, and mass = 7.84 gm. The experiments must, therefore, be interpreted with this in view. By using lighter coils we should have obtained results of the nature depicted by curve 3, fig. 13, and these would not have been so easy to interpret owing to the uniformity of output above 2000 cycles--i. e., the resonance is not sufficiently striking to contrast clearly at a particular frequency.

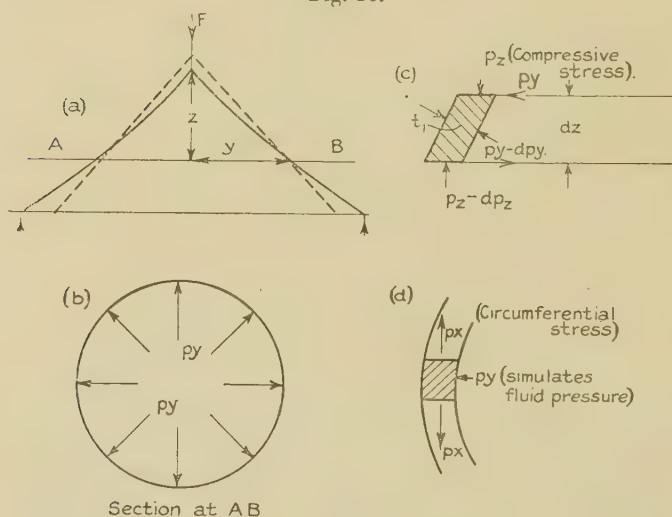
11. *Stresses in a Conical Sheet.*

To interpret the experimental results more readily it is essential to give a short account of the stresses in a conical sheet. The simple statical case where a vertical force F acts at the apex has been selected for consideration. Although in practice the force is applied by the coil to a frustum, the case illustrated in fig. 16 serves our present purpose. When $\psi = 180^\circ$, the cone degenerates into a flat disk and the forces are those due to bending and shear. When $\psi = 0$, the radius of the base remaining constant, we get a cylinder, and the stress is purely compressive. Between these two extremes the stresses are entirely different. The force acting obliquely at any horizontal section in fig. 16 can be resolved vertically and horizontally. The vertical force causes compression bending and shear, whilst the horizontal component simulates the fluid pressure in a boiler. It causes a circumferential tension which varies with the distance from the vertex. The variation in the radial force causes bending and shear, as shown in fig. 16. The cone, therefore, undergoes a vertical deflexion and a circumferential distension, ultimately taking up a curved shape of the form suggested by the full lines in fig. 16. Obviously, the relative magnitudes of the stresses depends upon the apical angle ψ .

Coming now to the experimental results, we find that the frequency of the first *radial* mode of a free-edge cone ($\psi = 90^\circ$) is dependent upon the thickness of the paper. This condition also holds for disks, so that here the action is mainly due to bending.

With a series of 90° cones the main symmetrical mode is almost independent of the thickness, which shows that bending is not then predominant. Moreover, one turns instinctively to the circumferential tension as a governing factor in the matter. If we imagine a cylindrical sheet to vibrate radially as a whole—not flexurally—the frequency

Fig. 16.



Diagrams illustrating the stresses in a conical sheet when a statical force is applied at the apex. The stress p_x is caused by circumferential tension. This tension varies from the apex downwards and in conjunction with p_z causes bending and shear. The deformed shape of the diaphragm (exaggerated) is indicated at (a). (c) is a portion of a section by a vertical plane, whilst (d) is a part plan of (c).

is independent of the thickness. This follows from the fact that the increase in mass is proportional to the increase in circumferential stiffness, *i. e.*,

$$\frac{\omega}{2\pi} \propto \left[\frac{\text{restoring force}}{\text{mass}} \right]^{1/2}.$$

Thus it appears that with apical angles of 90° the motion of the cone is largely radial and the stress circumferential.

As the angle approaches 180° , bending will become assertive, and ultimately the circumferential stress will vanish.

12. Experiments with Sheet Metal Cones.

We saw that the main symmetrical mode of the standard diaphragm occurs about 2000 cycles and that there is little sound output above 6000 cycles. The upper register might be extended by raising the frequency of this mode, and the problem now arises as to the method of procedure.

In all formulæ associated with the natural oscillations of a body, whatever its shape and mode of vibration, we encounter the factor $\left(\frac{E}{\rho}\right)^{1/2}$, i. e., the velocity of propagation of longi-

TABLE XII.
Showing Values of $\left(\frac{E}{\rho}\right)^{1/2}$ for various Materials.

Material.	E. Young's modulus (dynes cm. $^{-2}$).	ρ . Density (gm. cm. $^{-3}$).	$(E/\rho)^{1/2}$. Velocity in a uniform bar of material (cm. sec. $^{-1}$).
Paper	1.9×10^{10}	6.6×10^{-1}	1.7×10^5
Copper	1.25×10^{12}	8.9 „	3.7 „
Steel	2.0 „	7.9 „	5.0 „
Aluminium	7.2×10^{11}	2.7 „	5.1 „
Elektron	4.5 „	1.8 „	5.0 „

tudinal waves in a uniform bar of the material. Taking the values of E and ρ for the paper diaphragm of fig. 5, we find

$$\left(\frac{E}{\rho}\right)^{1/2} = 1.7 \times 10^5 \text{ cm. sec.}^{-1}.$$

From a book of physical constants we obtain the data given in Table XII. rows 2 to 5.

Here we see that $\left(\frac{E}{\rho}\right)^{1/2}$ is highest for aluminium and elektron metal, although the value for steel is somewhat similar. The latter can be ruled out, since for a given thickness an elektron cone is less than $\frac{1}{4}$ and an aluminium cone about $\frac{1}{3}$ the mass of one made of steel. Thus, if a diaphragm be constructed of elektron or aluminium, the frequency of its main mode will be some three times that

for paper—*i. e.*, about 6000 cycles. This should give a better upper register. For equal mass the aluminium should be about $\frac{1}{4}$ the thickness of the paper—*i. e.*, from 2 to 3 mils thick (0.005 to 0.0075 cm.).

Cones have been constructed using aluminium sheet 0.0025 and 0.0075 cm. thick, the dimensions and conditions being identical with those for Table III., case (c). The apparent radiation resistance was not measured, but tests were conducted on broadcast reception, using a high-quality receiver. With 0.0025 cm. sheet, the reproduction was accompanied by a loud crinkling sound, caused by heavy transients, break-up of the diaphragm on such occasions being visible to the naked eye. This defect was eliminated by a coat of thick aeroplane dope applied to each side of the cone. The reproduction was then quite pleasant, there being no resonances strikingly audible, but the upper register and the general output level were weak. Of course, by using a very low output level no crinkling occurred in the undoped state, but under this condition judgment of the quality was impossible. The lack of upper register was probably due (1) to the bass being relatively powerful owing to the rubber surround, (2) to the damping influence of the dope.

The 0.0075 cm. aluminium sheet had a much more powerful upper register, but the crinkling was absent. Speech was clear-cut and rather sharp, but there was no marked shrillness when reproducing sibilants—*e. g.*, the letter “s” did not whistle. A lack of “body” was evident, which suggested a weak register from about 200 to 2500 cycles. Increasing the loudness accentuated the bass and the register above 2500 cycles, but the reproduction was rather irritating and never full. This points to elevation of the main symmetrical mode from 2000 cycles to a higher frequency.

Before closing this section it is of interest to discuss the problem of multiple resonances which sometimes occur with paper cones.

Referring to Table VIII., it is seen that when $\psi = 60^\circ$ a cone 12 cm. radius has one resonance, whilst a cone 8.5 cm. radius has two resonances. Also, from Table IX., when $\alpha = 9.5$ cm. and $\psi = 135^\circ$, there are no fewer than four resonances, covering a frequency band of 350 cycles. It is impossible with the evidence at our disposal to state definitely the cause of multiple resonance. It was not obtained with $\psi = 90^\circ$, excepting as shown in Table XI., when the thickness of the paper was doubled or when a light flexible coil was used. The most probable cause is heterogeneity of the paper and the influence of the seam. In this respect radial modes occur at

more than one frequency. If E is found for a strip of paper cut in one direction, it may differ from that in another direction, and the values of ρ may follow suit. Since a cone is formed from a circular sector, $\left(\frac{E}{\rho}\right)^{1/2}$ may vary from generator to generator and from section to section. Thus, there may be more than one frequency at which the reflected energy is sufficient to cause an adequate portion of the cone to execute an abnormal amplitude. In other words, the whole cone does not resonate simultaneously.

13. *Measurement of apparent Radiation Resistance R_m .*

When a diaphragm is driven by a circular coil immersed in a magnetic field, there are four sources of resistive loss: (a) hysteresis and eddy current losses in the iron core, (b) copper loss in the coil, (c) mechanical loss in the diaphragm, supports, etc., (d) radiation of sound. The value of R_m is the difference between the resistances with the coil fixed and free, and includes items (c) and (d) plus a variable part due to the iron.

It is difficult to obtain R_m with accuracy by taking the difference between the readings with the coil free and fixed for the following reasons:—

1. It is almost impossible to have the coil in the same mean position for free and for fixed measurements unless the latter are obtained by using molten paraffin-wax to make a solid mass. This is particularly the case at the higher frequencies, as evinced by the lead-block experiment in section 7. Only a few microns represents a loud sound at 3000 cycles. By aid of paraffin-wax the sound can be eliminated entirely.

2. If the free and fixed measurements are made separately, it is imperative that the temperature of the coil should be identical in each case. The temperature coefficient of copper is 0.4 per cent per degree Centigrade. The temperature of the electro-magnet gradually rises with time owing to heating of the coil *, unless the current is maintained constant for some time. A variation in temperature of 15° C. can easily occur, with a consequent rise of 6 per cent. in the resistance of the coil. Thus, if the resistance free were measured, say, at the beginning of a day at 20° C. and the resistance fixed at 35° C. at the end of the day, the value of the latter would be 6 per cent. high. Under this condition low-frequency tests on a diaphragm with reinforced edge (R_m small) would

* This difficulty substantially disappears when a permanent magnet is used.

reveal a negative sound output, since the *actual* variation between the free and fixed resistance is less than 6 per cent. In the work described herein, the fixed and free measurements were taken at close time intervals after the magnet had attained a steady temperature*. The constancy of temperature can be checked by aid of d.c. bridge measurements.

3. The iron loss varies according as the coil is fixed or free, and when the output is small this usually results in $(R_1 - R_0) = R_m$ being negative at frequencies of the order of 4000 cycles and upwards.

In the present experiments no attempt was made to fix the coil by mechanical means. As explained in a former paper†, the fixed condition was simulated by short-circuiting the magnet on itself. The error incurred in the measurement of R_0 —due to the variation in iron loss with and without the field—was about 1 per cent.

Assuming actual fixation of the coil, we can consider a case where $(R_1 - R_0) = R_m$ is only 2 per cent. of R_0 . To obtain R_m to an accuracy of 1 per cent. it is necessary to measure R_1 and R_0 to $\pm 1/200$ th part of 2 per cent.—i. e., 1 part of 10,000. Apart from the first two sources of error enumerated above, the variation in iron loss entirely precludes any hope of attaining this degree of accuracy. When the diaphragm loss is added as a further complication, the difficulty of measuring the actual *sound* output from a reproducer of low efficiency by electrical means is evident.

A discussion of the variation in R_0 and L_0 with the field off and on may be of interest and use. When the coil is glued to the central pole of the magnet, R_0 is 1 per cent. higher for field on than for field off at 500 cycles. As the frequency rises the difference decreases, being zero at 1500 cycles. Thereafter it is actually negative, which illustrates the fickle character of the iron loss. Moreover, the values of R_m are in excess below 1500 cycles and in defect above this frequency. These variations are due to the superposition of a.c. upon d.c. magnetization. A similar result was found with a permanent magnet. In this case, using a diaphragm, with the coil actually fixed at the higher frequencies, the value of R_m was negative.

Some data are given in Tables XIII. and XIV. showing the resistance differences for two freely suspended coils—without a diaphragm—having 40 and 600 turns respectively, with the magnet winding energized and with it short-

* See Phil. Mag. xi. p. 1144 (June 1931).

† Phil. Mag. *loc. cit.*

circuited on itself. The radiation resistance under these conditions is very small indeed, and the tabulated results are a guide to the behaviour of the iron.

TABLE XIII.

Showing Difference in Resistance of Freely-supported 40-turn Coil of 28 s.w.g. with the Magnet Winding (a) energized; (b) short-circuited.

Frequency (cycles per second).	Difference in resistance (ohm).
0	0.0
50	+0.011
100	+0.028
150	0.0
200	0.0
250	+0.014

TABLE XIV.

Showing Difference in Resistance of Freely-suspended 600-turn Coil with the Magnet Winding (a) energized, (b) short-circuited.

Frequency.	Difference in resistance (ohms).
0	0
500	+16
1000	-25
1500	-35
2000	-35
2500	-35
3000	-33
5000	-29

In Table XIII. the difference in resistance starts from zero, passes through a maximum, and returns to zero, after which another maximum occurs, doubtless followed by transition to a negative value, as indicated in Table XIV.

14. *Method of detecting Miscalculated or Short-circuited Turns on a Coil.*

An interesting point arose in connexion with the 600-turn coil cited in the preceding section. It was labelled 700 turns,

but the error was detected in the following way. By plotting points the inductance in motion was found to be zero at a frequency of 710 cycles per second. As shown in a previous paper, the mass of the coil under this condition is given by $M_c = C^2/\omega^2 L_0$, where C^2 is the electromechanical conversion factor and L_0 is the static inductance in absolute units. Knowing the field strength H , the value of C can be calculated from the formula $2\pi r n H$. The measured value of L_0 was 5.7×10^7 absolute units (0.057 henry), giving $M_c = 5.46$ gm., whilst the value by weighing was only 4 gm. The increase in mass found by electrical measurement is due to C^2 being calculated on a 700-turn basis. Recomputing the coil on a 4-gm. basis, we find that $n = 600$ turns. From previous work it is known that the static inductance L_0 varies as n^2 . By reference to a standard 1000-turn coil, $L_0 = 1.56 \times 10^8$ abs. units (0.156 henry) at 710 cycles, so that 600 turns is represented by 5.7×10^7 , which is the value by measurement. Thus either the coil had 700 turns, some of which were short-circuited thereby making 600 of the remainder effective, or the turns were wrongly counted.

Obviously, the error could have been detected at once by reference to the 1000-turn coil, but in measurement of the accession to inertia it would be detected in the value of the total mass. Hence, the citation of this particular case. Clearly, it is advisable to measure the accession to inertia by aid of coils of silk-covered wire to avoid the possibility of short-circuited turns which vitiate the result.

15. *Apparent Efficiency, η_a .*

The apparent efficiency is defined as the ratio R_m/R_1 , where R_m is the apparent radiation resistance and R_1 is the effective resistance when the coil is free to move in air. We have already shown that R_m includes diaphragm losses, etc., and can only be found approximately. The results must therefore be interpreted with this in mind. Data for the diaphragm of fig. 9 are detailed in Table XV., whilst the corresponding values for a rigid disk of equal radius and mass are added.

The efficiency*—even after allowance for diaphragm loss—appreciably exceeds that of a rigid disk, which is very fortunate indeed, since a given output can be obtained with a power-valve of moderate capacity worked at low anode

* Since the values in the Table are fairly large, errors introduced in the measurement R_0 and R_1 due to variation in iron loss do not seriously affect R_m and η_a .

voltage. The rapid attenuation of output from the rigid disk above 1000 cycles due to interference is indicated in column 3.

The efficiency and the radiation resistance are only criteria of output when the *current is constant at all frequencies* *. To obtain the actual output it is necessary to multiply R_m by the square of the current, *i. e.* E^2/Z^2 , where E is the voltage impressed on the coil and Z is its impedance in motion.

TABLE XV.

Showing Apparent Efficiency of Coil-driven Conical Diaphragm with Rubber Surround at various Frequencies.

$a_1=12.2$ cm. ; $a_2=14$ cm. ; $l=0.3$ cm. ; $t_1=2.1 \times 10^{-2}$ cm. ;
 $t_2=10^{-2}$ cm. ; $t_3=1.6 \times 10^{-2}$ cm. ; $n=1200$ turns ;
 $\psi=90^\circ$; $M_c=4.7$ gm. ; $H=1.1 \times 10^4$ lines cm.⁻².

Frequency (cycles per second).	R_m . Apparent radiation resistance.		η_a . Apparent efficiency.	
	Cone in 6 ft. baffle.	Rigid disk in infinite baffle.	Cone in 6 ft. baffle.	Rigid disk in infinite baffle.
300	336	79	16.1	4.3
500	346	83	15.9	4.3
1000	396	59	18.3	Not calculated.
2000	192	15.6	7.9 (not a resonance)	0.69
3000	394	7.1	12.6	0.26

The values of Z are computed from measurements of R_1 and L_1 .

If the energy radiated by a rigid disk were constant at all frequencies, the axial pressure would increase considerably with rise in frequency above 1000 cycles. This follows immediately from the concentration of energy in the form of a beam †. Assuming the axial energy to be 1 unit at 300 cycles, where the distribution is equal in all directions, its value at any other frequency is found—for constant current

* Pentode power-valve condition.

† Proc. Roy. Soc. cxxii. pp. 604–609 (1929); also, ‘Wireless World and Radio Review,’ caption to fig. 5, p. 374, foot of column 1 and top of column 2, p. 375, March 30th, 1927. The formula used for these calculations was also used for curves in W. W., Sept. 21st, 1927, and is (17) of paper in Proc. Roy. Soc. It was obtained in May 1926, but publication was unfortunately delayed till 1929.

conditions—by the inverse ratio of the resistances. This is set down in Table XVI., column 2. On the assumption that the energy distribution from the conical diaphragm is identical with that from the rigid disk, the computed axial energy is given in column 3. These data have been reproduced in decibel units in the last two columns of Table XVI.

TABLE XVI.

Showing Energy on Axis of Rigid Disk for equal Sound Output at all Frequencies, compared with that from the actual Reproducer of fig. 9.

Frequency (cycles per second).	Ratio of axial energy to that at 300 cycles.		Ratio on decibel basis.	
	Rigid disk in infinite baffle.	Cone in 6 ft. baffle.	Disk.	Cone.
300	1.0	1.0	0	0
500	1.0	1.0	0	0
1000	1.34	1.58	1.3	2.0
2000	5.06	2.9	7.0	4.6
3000	11.1	13.0	10.5	11.0

The output from the cone reproducer is fairly uniform (on a decibel basis) when the listener is suitably situated in an ordinary room, but listening on the axial line is unpleasant, owing to preponderance of the upper register. The axial pressure ratio is obtained by taking the square root of the quantities in column 3. For example, at 3000 cycles it is $(13)^{1/2} = 3.6$. Moreover, characteristic curves of loud speakers showing the axial pressure convey no idea of the results obtained in practice*. A curve showing the total energy radiated at all frequencies—irrespective of focussing—throughout the acoustic register is the desideratum. Of course, by plotting the actual axial characteristic alongside the axial pressure curve for equal output at all frequencies, some idea of the real performance could be gained. Allowance, however, would have to be made for interference effects on the axis of the reproducer.

* Assuming the external conditions to be suitable and identical in all cases.

16. Conclusion.

The experimental evidence shows that when the edge of a diaphragm is reinforced (no surround) to prevent radial modes at low frequencies, the lower register appears to be missing. This is due to enhanced output in the upper register, resulting from resonances which mask the lower register. Thus, although the diaphragm, whether disk, cone, or other shape, may behave as a rigid structure at low frequencies, it breaks up at the higher frequencies. To equalize the output it is imperative to introduce a resonant member to assist the lower register. One method of achieving this is to suspend the diaphragm from an annulus of suitable material, dimensions, and radial tension. The annulus acts as an auxiliary resonant diaphragm at low frequencies and effects a considerable improvement in the reproduction. The magnetic field should be as intense as possible to impose a high degree of damping on the natural oscillations of the system. As an alternative, the upper register can be attenuated to the same degree as the lower register, but this is accompanied by a large reduction in the general output level.

The scope of the upper register for any given size of cone is limited by the material, whose properties govern the frequencies and magnitudes of the resonances, the latter depending upon transmission loss. The upper register is augmented by the use of coils of small mass. The main symmetrical mode is substantially independent of the thickness of the material. It is dependent upon $(E/\rho)^{1/2}$. Thus, the upper register might be improved by using a material having a higher value of $(E/\rho)^{1/2}$. This points to the use of thin sheet metal (about 7.5×10^{-3} cm.) or other material of suitable mechanical properties.

Experiments with thin aluminium sheet have, however, not been crowned with success, since a large portion of the register above 200 cycles is relatively weak. The reproduction lacks body and is aurally unpleasant. This emphasises the difficulty in obtaining a uniform register of wide compass from a system where resonances abound and the acoustic loading is small. In the exponential horn type the acoustic (resistive portion) loading is relatively high and gives large damping. It is a scientific but at the moment not an economic solution to the problem of sound reproduction!

17. *Appendix.*

TABLE XVII.

Showing Resonances of Conical Diaphragm with Presspahn Ring 2.5 cm. wide, 3.2×10^{-2} cm. thick, glued to edge (ρ for presspahn = 1.0 gm. cm.^{-3}).

$$a_1 = 12.2 \text{ cm.}; t_1 = 2.1 \times 10^{-2} \text{ cm.}; t_2 = 2.4 \times 10^{-2} \text{ cm.}; \\ l = 2.5 \text{ cm.}; \psi = 90^\circ; M_c = 7.84 \text{ gm.}; \text{no baffle.}$$

Frequency (cycles per second).	R_a (ohms).	Remarks.
70	0.031	Reduction of presspahn to a width 0.8 cm. eliminated the resonance at 205 cycles. The main resonances were then 900 cycles ($R_m = 0.18 \text{ ohm}$) and 2000 cycles ($R_m = 0.44 \text{ ohm}$). The increase in R_m at 2000 is not necessarily due to the variation in the edge condition. It is probably due to variation caused by secular changes, as this test was conducted 10 days later. A fortnight later still, R_m was 0.32 ohm at 2200 cycles.
110	0.012	
155	0.035	
205	1.47	
800	0.1	
1000	0.11	
1400	0.105	
2000	0.31	
3250	0.1	

TABLE XVIII.

Showing Resonance Frequencies corresponding to figs. 7 and 9.

$$a_1 = 12.2 \text{ cm.}; a_2 = 14 \text{ cm.}; t_1 = 10^{-2} \text{ cm.}; t_2 = 2.1 \times 10^{-2} \text{ cm.}; \\ l = 0.3 \text{ cm.}; \psi = 90^\circ; M_c = 4.7 \text{ gm.}$$

Diaphragm doped and used in baffle 6 ft. square.

Frequency (cycles per second).	R_a (ohms).
118.3	539
129.5	830 (surround <i>per se</i>)
175	240
190	241
250	225
350	222
650	192
800	194
950	209
1550	91
1750	82
2450	197
2900	213
3200	201

TABLE XIX.

Showing Static Inductance L_0 , Static Resistance R_0 , and Effective Permeability μ_e with 40-turn and 1000-turn Coils

Air-gap=0.32 cm.; Coil temp.=20° C.; inductance of 40-turn coil in air= 1.32×10^{-4} henry; ditto 1000-turn coil= 8.3×10^{-2} henry; D.C. resistance of 40-turn coil=0.95 ohm (no leads); ditto 1000-turn coil=1257 ohms.

Mean radius of coil=2.5 cm.

Axial length of coil=0.95 cm.

Frequency (cycles per second).	L_0 . Inductance of coil with field short-circuited (henry).		R_0 . Resistance (ohms).	Added resistance due to iron (ohms).	μ_e . Effective permeability of electromagnet.	
	40 turns.	1000 turns.			40 turns.	1000 turns.
50	3.22×10^{-4}	2.21×10^{-1}	1388	131	2.44	2.66
100	3.0	2.1	1395	138	2.28	2.53
150	2.86	1.98	1403	146	2.16	2.38
200	2.78	1.91	1412	155	2.1	2.3
500	2.48	1.65	1460	203	1.88	1.99
1000	2.22	1.49	1570	313	1.68	1.8
2000	2.06	1.34	1800	543	1.56	1.61
3000	1.94	1.25	2200	943	1.47	1.51
4000	1.8	1.19	2750	1493	1.36	1.43
5000	1.7	1.12	3500	2243	1.29	1.35

The inductances of the coils out of the magnet are almost exactly proportional to the squares of the number of turns. Since the magnetizing force on the iron is greater with 1000 than with 40 turns, the inductance per turn of the former exceeds that of the latter. The air-core ratio is 628/1—it should be 625/1 for the inductance to vary absolutely as n^2 ,—whilst in the magnet it varies from 687/1 at 50 cycles to 659/1 at 5000 cycles. The variation in effective permeability is obviously identical. The resistance of a 40-turn coil is not given, since the short coil-leads were removed before being accurately known. The ratio of the resistances due to iron loss, however, is greater than that for inductances, since the former depends upon B^x , $x > 1$, whilst the latter depends upon B , the a.c. flux density in the iron.

Measurement of Accession to Inertia (M_1) when a Diaphragm does not move as a whole.

The methods of measuring M_1 described previously* only apply when the diaphragm moves as a whole. This hypothesis ceases to be true above about 400 cycles per second, owing to "break-up" occurring. The method to be used at higher frequencies is based on previous work†. At any particular frequency an electrical circuit can be represented by an inductance in series with a resistance. Similarly, a mechanical structure can be represented by a mass and a mechanical resistance in series.

When a mechanical driver is associated with simple elastic constraint, the resonant or forced frequency depends upon the total mass, but not upon the resistance to motion. This is analogous to an LC circuit, where the criterion $\omega^2 LC = 1$ is independent of resistance, which only affects the "free" period (components in series).

In a moving-coil reproducer, suitable elastic constraint can be introduced by a centering device having a linear force/displacement relationship. By aid of a bridge method as described herein, the resonance frequencies of such an arrangement are found in air and *in vacuo*, when the spring or some suitable part of the moving structure is loaded with various masses. The loading must not introduce local break-up of the diaphragm. Using the same or a similar coil and centering device *without the diaphragm*, the process is repeated. Added mass is plotted against a frequency base, and three curves are obtained. At any particular frequency let m_1 , m_2 , be the added masses in air and *in vacuo* with the diaphragm attached, and m_3 the added mass without the diaphragm in air. Then the accession to inertia $M_1 = (m_2 - m_1)$. The effective mass of the diaphragm in air (including M_1 but excluding the coil) is $(m_3 - m_1)$, and the effective mass *in vacuo* is $(m_3 - m_2)$. In measuring m_3 in air it is assumed that M_1 is negligible. If this is invalid, the values of m_3 must be found *in vacuo*.

The value of M_1 found in this way invites criticism. By taking $M_1 = (m_2 - m_1)$ it is assumed that the "shape" as well as the amplitudes of the various vibrating areas into which the diaphragm breaks up are identical in air and *in vacuo*. When the acoustic load and the accession to inertia at or near a prominent resonance is removed, *i. e.*, measurement *in vacuo*, the amplitude and the shape alter. This does

* Phil. Mag. pp. 1137-1152 (June 1931).

† Phil. Mag. pp. 12-16 (Jan. 1931), also p. 1151 (June 1931).

not apply to the effective mass in air ($m_3 - m_1$). Although the results obtained for M_1 are approximate, they may be of value in certain cases. They are accurate at low frequencies where the diaphragm moves as a whole.

The above procedure can obviously be applied to an electromagnetically operated reed movement. In both coil and reed drives a number of elastic elements with different natural periods will be required to cover a wide frequency band. The method is, of course, applicable at any frequency, whether the diaphragm moves as a whole or not.

March 1931.

LXXVIII. *The Excitation of the Visible Spectrum of Helium.*—II. By J. S. TOWNSEND, M.A., Wykeham Professor of Physics, Oxford, and F. LLEWELLYN JONES, B.A., Senior Demy of Magdalen College, Oxford*.

1. **I**N our first paper† we described some experiments which were made to determine the variations in the intensity of the light in different parts of the spectrum of discharges through helium due to variations in the pressure of the gas. We also indicated a method of finding the mean energies E of the electrons which excite radiation from observations of the intensities of the light obtained with a given current in the gas at different pressures. The theory of this method depends on a series of investigations that have been made of the motion of electrons in gases‡, and it may be applied to compare the energies of the electrons which excite radiation with the energies of the electrons in the collisions with atoms that are ionized§.

The results which have already been given were deduced from experiments with direct-current discharges, where the changes in the intensity of the radiation was measured by the effect of the light on the resistance of a selenium cell.

Other experiments have since been made in which the intensity of the light was determined by different methods, and in some cases high-frequency discharges were used instead of direct currents.

* Communicated by the Authors.

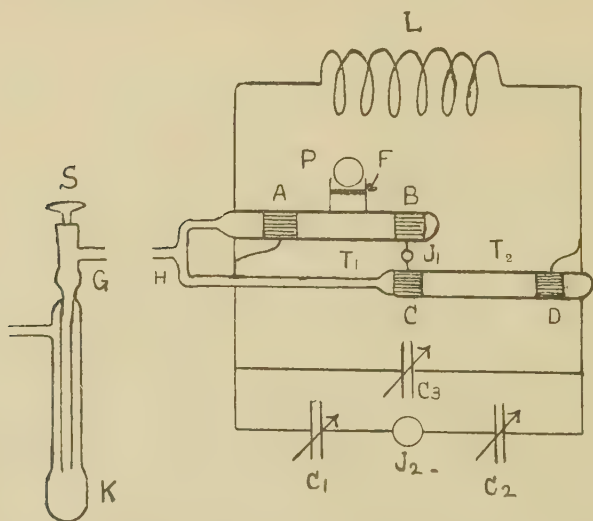
† J. S. Townsend and F. Llewellyn Jones, *Phil. Mag.* xi. p. 679 (March 1931).

‡ 'Motions of Electrons in Gases' (Clarendon Press, Oxford, 1925).

§ J. S. Townsend, *Phil. Mag.* ix. p. 1145 (June 1930) and *Phil. Mag.* xi. p. 1112 (May 1931).

In this paper we propose to give an account of the experiments with high-frequency discharges in helium in which the light in different parts of the spectrum was measured by photoelectric cells.

2. The high-frequency current passed through two quartz tubes T_1 and T_2 arranged symmetrically in an oscillatory circuit as shown in the figure. The currents and forces were measured by the method which had been used in another investigation*. The inductance L of the circuit was loosely coupled to a continuous wave generator. The wave-length used in most of the experiments was 84 metres. The high-frequency potential was applied to the tubes by the sleeves



A and D. The sleeves B and C were connected together through a thermojunction J_1 which was at a potential node. The same current passed through the two tubes, and there was no current in the thermojunction J_1 due to oscillations in the circuit except when the luminous discharge appeared in the tubes. It was found that small currents could be measured accurately by this arrangement. The potential difference between the sleeves A and D was measured by the current through the condensers C_1 and C_2 .

The tubes T_1 and T_2 were of the same size, 30 centimetres long and 3.4 centimetres internal diameter, and were con-

* J. S. Townsend and W. Nethercot, *Phil. Mag.* vii. p. 599 (March 1929).

nected by narrow quartz tubing 70 centimetres long and 6 millimetres in diameter, through a glass tap S, to the glass tube K containing charcoal. One end of the narrow quartz tubing was sealed to the tube H and the other end was ground to fit the glass tubing G near the tap S, and the junction was made airtight by hard elastic cement. The quartz was heated to a high temperature (about 700 degrees C.), and the tubes were washed out with pure gas in order to remove impurities given off from the surface. During this process the tube K was cooled with liquid air and the tap S was open. It was found that all traces of impurities were removed when this operation was repeated two or three times. The apparatus was subsequently tested by introducing pure helium and leaving it in the tubes for about a month, with the tap S closed.

The force required to maintain a current and the intensities of the light in different parts of the spectrum when a given current passed through the tubes were measured immediately after the gas was admitted and at intervals of some weeks. No change in any of these quantities was detected, and throughout the whole time it was impossible to see any lines in the spectrum of the gas except those due to helium. The same results were obtained with different specimens of gas.

It was thus found that there was no necessity for a trap cooled with liquid air to be placed between the tap S and the tubes T_1 and T_2 in order to prevent the diffusion of impurities from the tap-grease into the quartz tubes. The long narrow quartz tubing retards the diffusion, and the impurities are absorbed by the tubing, which had been heated *in vacuo* for some hours.

The light from one of the tubes was measured by a photoelectric cell P, which was fixed at a distance from the tube so as not to disturb the discharge. The light passed through a filter F, and the cell was screened, so that it only received light from the centre of the luminous column, where the force is uniform, and no light from parts of the gas near the electrodes fell on the cell. Four light filters were used in order to examine the light in different parts of the spectrum. The red filter admitted light of wave-lengths between 6200 Å. and the red end of the visible spectrum. Thus with this filter the photoelectric current was principally due to the red line $\lambda = 6678$ Å. With the yellow filter the yellow line $\lambda = 5876$ Å. was transmitted. The green filter transmitted the three lines $\lambda = 5048$ Å., 5016 Å., and 4922 Å. The line $\lambda = 5016$ Å. was much the brightest of these, so that

the photoelectric effect of the light passing through the green filter was principally due to this line. With the violet filter lines of wave-lengths between $\lambda=4850 \text{ \AA.}$ and the violet end of the visible spectrum fell on the cell, the principal lines being $\lambda=4713 \text{ \AA.}$ and $\lambda=4471 \text{ \AA.}$

3. At each pressure the photoelectric effect of the light of any colour was proportional to the current, and the light of any colour due to a given current diminished as the pressure was increased from 1 millimetre to 38 millimetres.

At pressures greater than 20 millimetres the discharge tends to become striated as the current is increased. This effect is noticeable with a current of about 10 milliamperes, but with smaller currents the luminous column is uniform*. At pressures less than 13 millimetres the discharge is

TABLE I.

p .	Z .	Z/p .	R.	Y.	G.	V.
38	43	1.13	10	10	10	10
23	32.2	1.40	14	16.2	11.0	10.8
13	20	1.54	26	36	16	15
7.2	12.3	1.70	33	54	20	20
3.7	6.6	1.80	44	85	34	37
2.8	5.6	2.0	48	100	42	45
1.0	3.4	3.4	78	127	107	91
.6	3.25	5.4	83	115	200	120
.42	2.85	6.8	98	100	260	140
.235	14.5	62	60	56	420	130

not striated for currents between 1 and 15 milliamperes. In this respect the high-frequency discharge differs from the direct-current discharge, as striations are obtained with direct currents at pressures less than about 2 millimetres †.

The results of the experiments are given in Table I. The pressures p of the helium in the quartz tubes are given in millimetres of mercury and the force Z in the uniform luminous column in volts per centimetre. The photoelectric currents due to the light admitted to the cell through the red, yellow, green, and violet filters are given in columns R, Y, G, and V respectively. The figures in these columns represent the intensity of the light obtained with a current of 5 milliamperes through the discharge-tube. In each case

* The striations obtained with large pressures were also observed by Hayman (R. L. Hayman, *Phil. Mag.* vii. p. 586, March 1928).

† F. Llewellyn Jones, *Phil. Mag.* xi. p. 163 (January 1930).

the intensity of the light obtained with the pressure of 38 millimetres is taken as 10.

From this table it is seen that the most noticeable changes in the intensity of light as the pressure is reduced are those of the yellow and the green lines. At pressures below 1 millimetre the intensities of the light through the red and yellow filters passes through a well-marked maximum value, while that of the green lines increases continuously as the pressure is reduced to .235 millimetres.

The results show that all the principal lines (of wavelengths 6678, 5896, 5016, 4713, and 4471 Å.) become brighter as the pressure is reduced from 38 millimetres to 1 millimetre, and the rate of increase of the intensity of the lines with the pressure is much greater than that of the ratio Z/p .

4. These results may be explained on the hypothesis that the radiation is due to collisions of electrons with atoms of the gas in which the energies E_x of the electrons is much greater than the mean energy E_1 , since a small change in the value of E_1 causes a great change in the number of electrons with energies greater than E_x .

The mean energy of agitation E_1 of electrons has been determined accurately in terms of the ratio Z/p by experiments on the lateral diffusion of a stream of electrons, and for a range of values of Z/p from 1.2 to 2 the value of E_1 in volts is almost exactly $2Z/p$ for helium.

If the distribution of the energies of the electrons about the mean value E_1 were known, the energies of the electrons which excite radiation in different parts of the spectrum could be determined approximately.

5. The following considerations are of interest in considering the distribution of the energies.

When the mean energy E_1 of the electrons is not much greater than that of the gas, *i. e.*, about 1/20th volt, it may be assumed that the distribution of the energies about the mean value is approximately the same as the Maxwellian distribution.

In an electric field the actions which give rise to the Maxwellian distribution diminish in importance as the intensity of the field increases.

There are, however, other actions which increase in importance and give rise to another distribution of the energies of the electrons. Some electrons acquire energies greater than the mean energy by diffusing in the direction of the electric force, and others have their energies reduced

by diffusing in the opposite direction. A formula for the distribution of the energies due to effect of diffusion in an electric field has been derived in a previous paper*. The result may be expressed in the form

$$N_x/N = \phi(E_x/E_1), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N is the total number of electrons, E_1 their mean energy of agitation, and N_x the number of electrons with energies exceeding E_x .

For values of E_x greater than E_1 , $\phi(E_x/E_1)$ is given by the integral

$$\pi^{-\frac{1}{2}} \int_{E_x/E_1}^{\infty} e^{-(E/E_1 - .85)^2} d(E/E_1).$$

It is therefore of interest to calculate the energies of the electrons that excite different lines, taking the distribution of the energies to be given by the above formula, and to

TABLE II.

Filter.	Excitation energies in volts for pressures		
	38 to 13 mm.	13 to 2.8 mm.	2.8 to 1 mm.
Red.....	5.6	8.6	9.7
Yellow ...	6.2	9.0	9.2
Green	4.0	9.0	11.0
Violet	4.0	9.2	10.0

compare the results with those obtained by assuming the distribution to be the same as the Maxwellian distribution.

For values of E_x greater than E the formula for the ratio N_x/N , obtained from Maxwell's distribution, is approximately

$$N_x/N = A\sqrt{E_x/E_1} e^{-3E_x/2E_1}, \quad . \quad . \quad . \quad . \quad (2)$$

and this formula may be taken to find the energies E_x .

5. The range of pressures from 38 to 1 millimetre may conveniently be divided into three parts:—38 to 13 millimetres, 13 to 2.8 millimetres, and 2.8 to 1 millimetre. The energies of excitation in volts of the light which passed through the various filters for these three ranges of pressure are given in Tables II. and III.

The numbers in Table II. are obtained by taking the ratio N_x/N given by equation (1), and those in Table III. by taking the ratio N_x/N given by equation (2).

The method of obtaining the energies E_x from the intensities of the light, which are given in Table I., has been explained in the previous paper.

* J. S. Townsend, Phil. Mag. ix. p. 1145 (June 1930).

For the ranges of pressures below about 13 millimetres the spectrum of the light from the centre of the uniform luminous column consisted of the simple line spectrum of helium. It may therefore be assumed that the photoelectric effect of the light which passed through the filters was almost entirely due to the principal lines mentioned above in section 2. Thus the excitation energies for the light passing through the red filter, given in the third and fourth columns of Tables II. and III., apply approximately to the prominent red line given in section 4.

From the figures given in the tables, it is seen that the energies of the electrons which excite any given line increase when the mean energy of all the electrons is increased. This would not occur if there were a very high probability of the electrons exciting the atoms when their energy attained a certain critical amount. Thus it would appear that the probability of excitation depends on the energy of the

TABLE III.

Filter.	Excitation energies in volts for pressures		
	38 to 13 mm.	13 to 2·8 mm.	2·8 to 1 mm.
Red.....	11·6	19·5	21·6
Yellow ...	13·5	22·4	19·5
Green	8·7	22·3	26
Violet	8·5	23	24

electron in the collision with the atom which is caused to radiate.

6. The interpretation of the results given in the first column of Tables II. and III. is more difficult. For the higher range of pressures from 13 to 38 millimetres the helium band spectrum could be detected with large currents. The bands appeared principally in the neighbourhood of the electrodes, but they were also seen in the uniform luminous glow. The band spectrum was always much less intense than the line spectrum, but the band spectrum may have contributed to the photoelectric current. It seems highly probable that the band spectrum was due to molecular helium in the positive column of the discharge tube. Thus throughout the range of pressure from 13 to 38 millimetres the light which traversed the various filters was not entirely due to the line spectrum of atomic helium, which was the case for the lower pressures. Consequently the excitation energies given in the first column of the tables represent the average energies of the electrons in

the collisions with both atoms and molecules of helium which are caused to emit radiation. It is noticeable that these energies of excitation are much lower than those obtained with the ranges of pressures from 13 millimetres to 1 millimetre.

7. In the calculations of the energies of the electrons in collisions which cause atoms to radiate, the effects of the large losses of energy in these collisions have been neglected in the formulæ (1) and (2) for the distribution of the energies. The effect of these losses increases in importance as the mean energy E_1 increases, so that the formulæ which have been given for the distribution would probably be very inaccurate for pressures below 1 millimetre where the mean energy of the electrons is greater than 6 volts.

These large losses may also have an appreciable effect on the distribution when the mean energy is less than 5 volts, so that for this and other reasons it would be difficult to obtain an accurate formula for the distribution. Thus, although the formula for the distribution due to diffusion is only a first approximation, it is probable that the true distribution is represented more accurately by equation (1) than by equation (2). The figures in Tables II. and III. show that the values of the energies obtained by this method depends on the distribution, and as equation (1) is only an approximation the absolute values of the energies cannot be determined very accurately.

The results, however, show that the relative values of the excitation energies for the different lines, and the changes in these energies with the pressure, as obtained by this method of investigation are to a great extent independent of the formula for the distribution.

8. In conclusion, it is of interest to consider in a simple manner whether an alternative theory of the excitation of the helium spectrum, based on the properties of metastable atoms, can explain the results of these experiments. On this theory excitation occurs as the result of two successive impacts. After a collision in which the energy of the electron is about 20 volts the normal atom is raised to a meta-table state, and this atom radiates after a second collision in which the energy of the electron is about 3 or 4 volts.

As the energies of the electrons are distributed about the mean energy the number of electrons with energies about 3 or 4 volts when the mean energy is about 4 volts, is much greater than the number of electrons with energies exceeding

20 volts. Also, when the mean energy of the electrons is increased from 3 to 5 volts the number of electrons with energies exceeding 20 volts is greatly increased, while the increase in the number of electrons with energies between 3 and 4 volts is comparatively small.

Thus the change in the number of electrons which have sufficient energy to cause metastable atoms to radiate is comparatively small when the pressure of the gas is changed from 13 millimetres to 1 millimetre. Hence the intensity of the radiation of any particular wave-length is nearly proportional to the rate at which metastable atoms are formed.

The change of the intensity of the light when the pressure is reduced from 13 millimetres to 1 millimetre should therefore be approximately the same as the change in the number of electrons with energies exceeding 20 volts when the mean energy is raised from 3 to 5 volts. It follows, therefore, on this theory that the excitation energies calculated by the method used above should be nearly 20 volts, and should be very nearly the same for all wave-lengths. This conclusion is contrary to the facts, since the change of intensity of the lines when the pressure is reduced is different for the different lines. The experiments indicate that it is much more probable that the light in the uniform column of the discharge is due to single impacts of electrons with normal atoms of the gas.

LXXIX. *The Raman Effect in some Acid Derivatives and Esters.* By V. N. THATTE, Assistant Professor of Physics, College of Science, Nagpur, and A. S. GANESAN, M.A., Ph.D. (London) *.

[Plate XVI.]

THE liquids whose Raman Spectra are reported in this paper are the acid derivatives acetic anhydride, monochlor acetic acid, dichlor acetic acid, and trichlor acetic acid, and the esters amyl nitrate (iso), allyl isothiocyanate, ethyl oxalate, and the acetyl and benzoyl chlorides. The liquids were slowly distilled in vacuum and were contained in Wood's tubes. The mercury arc was used as the source, and the spectrograms were taken with a Hilger E₂ Quartz Spectrograph on Ilford Golden

* Communicated by the Authors.

Iso-zenith plates suitably backed. The mono- and the tri-chlor acetic acids were studied in aqueous solutions. Where the liquids showed fluorescence with the consequent continuous spectra masking the Raman lines, the incident light was filtered through a solution of quinine sulphate to cut out the ultra-violet portions of the mercury arc.

The results are given in Tables I.–VII. The intensity was estimated visually, taking the line that is just clearly visible on the negative to be of intensity (0). Where the

TABLE I.
Acetic anhydride, $\text{CH}_3\text{CO.O.CO.CH}_3$.

Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in vacuum.	Inten- sity.			
4999.5	(3)	20002	4358.3 (22938 cm. ⁻¹)	2936
4728.8	(0 <i>d</i>)	21147	"	1791
4647.7	(0)	21516	"	1422
4612.7	(0)	21679	"	1259
4596.9	(3)	21754	4046.6 (24705 cm. ⁻¹)	2951
4515.4	(1)	22146	22938	792
4491.3	(2)	22265	"	673
4430.6	(1)	22570	"	368
4296.5	(0)	23275	24705	1430
4182.9	(0)	23907	"	798
4160.8	(2)	24034	"	671

$\Delta\nu$...	368	672	795	1259	1426	1791	2944
$\lambda(\mu)$...	27.2	14.9	12.6	7.94	7.01	5.58	3.40
* Acetic acid $\Delta\nu$...	362	623	766	1280	1433	...	2944
(Intensity) ...	(1)	(3)	(0)	(2)	(3)	...	(5)

* Ganesan and Venkateswaran, Indian Journ. Phys. v. p. 216 (1929).

lines appeared diffuse and broad they are indicated by the letter *d*. At the foot of each table is given a subsidiary table, where the first row of figures indicate the Raman shifts observed and the second row the reciprocal of these giving the corresponding infra-red frequencies expressed in μ .

Acetic Anhydride.—The Raman spectrum of this liquid is very similar to that of acetic acid. All the frequencies,

except one, of the acetic anhydride are present in acetic acid though slightly shifted. The most prominent of these frequencies is 2944, which has the same value in both the liquids. This shift is characteristic of all the aliphatic compounds, but its structure varies with the liquid under examination. Thus in acetic acid this band really consists of three lines, the central line being sharp and the most intense, and those on either side of it being more diffuse. In the anhydride this is a simple and sharp line. The very prominent frequency 901 of the acetic acid is not present

TABLE II.
Dichlor acetic acid, CHCl_2COOH .

Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in vacuum.	Inten- sity.			
4692.4	2d	21311	4358.3 (22938 cm. ⁻¹)	1627
4650.9	2d	21501	"	1437
4605.9	2d	21711	4046.6 (24705 cm. ⁻¹)	2994
4538.4	1	22034	22938	904
4515.4	1	22146	"	792
4493.7	1	22253	"	685
4443.4	3	22505	"	433
4414.0	1	22655	"	283
4397.3	0	22741	"	197
4278.0	0	23375	"	-437
$\Delta\nu \dots$	197 283 433 685 792 904 1437 1627 2994			
$\lambda(\mu) \dots$	50.8 35.3 23.1 14.6 12.6 11.1 6.96 6.15 3.34			

in the anhydride, but instead we have a new diffuse line corresponding to 1791, which is nearly double the acid frequency shift, and this is also very strong in the infra-red absorption spectrum which has been studied by Bennett and Daniels*. The chief infra-red absorption bands are at 2.7 (strong), 4.1, 4.4, 4.75 (weak), and 5.5, 5.6 μ (strong).

Chloracetic Acids.—Of the three chloracetic acids, the dichlor acetic acid, being liquid at the ordinary temperature, gave the best Raman spectrum with well-defined

* Bennett and Daniels, J. A. C. S. xlix. p. 50 (1927).

lines. The other two acids were examined in aqueous solutions, and the water bands and also the tendency in these substances to get hydrolyzed, which resulted in giving a general background, impaired the definition of the Raman lines, and only the strongest of these could be measured with any degree of accuracy. In dichlor acetic acid the most prominent line is λ 4443.4 which corresponds to a frequency shift 433. There is also the anti-Stokes's line corresponding to this shift. In the other two compounds this frequency

TABLE III.
Amyl nitrate (iso), $C_5H_{11}NO_3$.

Modified lines.		Wave-number cm. $^{-1}$.	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.			
Wave-length in vacuum.	Inten- sity.						
5011.2	} 2d	19955	4358.3 (22938 cm. $^{-1}$)	2983			
4983.2		20067	"	2871			
4693.1	0	21308	"	1630			
4655.0	1	21482	"	1456			
4620.6	2	21642	"	1296			
4600.3	} 2d	21738	4046.6 (24705 cm. $^{-1}$)	2967			
4588.6		21793	"	2912			
4532.9	1	22061	22938	877			
4458.0	0	22432	"	506			
4302.7	1	23241	24705	1464			
4284.4	0	23340	"	1365			
4269.4	1	23422	"	1283			
4196.3	0	23830	"	875			
$\Delta\nu$	506	876	1290	1365	1460	1630	2927
$\lambda(\mu)$	19.8	11.4	7.75	7.33	6.85	6.13	3.42

is very weak. In trichlor acetic acid the next shift, 685, is stronger. The frequency 2994 is present in all the three acids as a diffuse band. In dichlor acetic acid this band extends over about 40 wave numbers and is intense on the red side shading towards the violet. The variation in the structure of this band with the successive substitution of the chlorine atom in acetic acid could not be examined, as in the aqueous solutions studied the broad water bands also occur in about the same position. This difficulty can be obviated if the spectra are taken in solutions of carbon

tetrachloride, and experiments in this direction are in progress. The infra-red spectra of these liquids have been studied by Bennett and Daniels (*loc. cit.*). The chief bands are located at 3 to 3.5 μ , 5.8 μ , 7.1 μ , and 7.6 μ .

Amyl Nitrate (iso).—The prominent lines in the scattered spectrum of this liquid are again what correspond to the aliphatic C-H bond. Their mean value is 2930 and the line is

TABLE IV.
Allyl isothiocyanate, C₃H₅NCS.

Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in vacuum.	Inten- sity.			
4994.5	(2 <i>d</i>)	20022	4358.3 (22938 cm. ⁻¹)	2916
4975.9	(1)	20096	"	2842
4795.5	(1 <i>d</i>)	20853	"	2085
4697.4	(3)	21288	"	1650
4649.6	(2 <i>d</i>)	21507	"	1431
4629.9	(2 <i>d</i>)	21598	"	1340
4618.8	(1 <i>d</i>)	21651	"	1287
4611.6	(1) }	21684	"	1254
4591.0	(1 <i>d</i>)	21782	4046.6 (24705 cm. ⁻¹)	2923
4575.8	(0)	21854	"	2851
4540.8	(1 <i>d</i>)	22022	22938	916
4498.8	(3)	22228	"	710
4468.9	(1)	22377	"	561
4436.6	(0)	22540	"	398

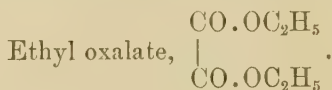
$\Delta\nu$... 398 561 710 916 1254 1287 1340 1431 1650 2085 2846 2920
 $\lambda(\mu)$... 25.1 17.8 14.1 10.9 7.98 7.78 7.46 6.99 6.06 4.80 3.51 3.42

very diffuse, extending over 80 wave numbers. A fact that is of considerable interest is the absence of the shift 1045. It is well known that this shift is characteristic of the NO₃ group and is present in all the nitrates *. It corresponds to the symmetric oscillation of the three oxygen atoms about the nitrogen, which mode of vibration does not give rise to a resultant dipole moment, and as such this frequency is optically inactive and absent in the infra-red spectra of

* Krishnamurti, Ind. Journ. Phys. v. p. 1 (1930).

nitrate but very conspicuous in their Raman spectra. In nitric acid* this shift is the strongest, and the variation in the intensity of the corresponding line with dilution has been studied by I. R. Rao†, who attributes this frequency to the NO_3 ion. In long chain compounds it may be that this free oscillation of the ion is damped, owing to the influence

TABLE V.



Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.				
Wave-length in vacuum.	Inten- sity.							
5011·5	(1)	19954	4358·3 (22938 cm. ⁻¹)	2984				
4722·2	(2)	21177	"	1761				
4654·7	(2)	21484	"	1454				
4603·7	(2) }	21722	4046·6 (24705 cm. ⁻¹)	2983				
4594·8	(2)	21764	"	2941				
4583·2	(1)	21819	22938	1119				
4563·8	(1)	21912	"	1026				
4547·1	(0)	21992	"	946				
4530·7	(3)	22072	"	866				
4421·2	(2)	22618	"	320				
4300·9	(1)	23251	24705	1454				
4194·8	(1)	23839	"	866				
4096·8	(1) }	24409	3650·1 (27389 cm. ⁻¹)	2980				
4090·0	(1) }	24450	"	2939				
$\Delta\nu$	320	866	946	1026	1119	1454	1761	2940-2983
$\lambda(\mu)$	31·2	11·6	10·6	9·75	8·94	6·88	5·68	3·41-3·35

of the other atoms, which may account for its absence in amyl nitrate (iso). Yet the strong shift 1305† of the nitric acid is also strongly represented here as 1296. It will be interesting to study the behaviour of this shift, 1045, in alcoholic solution where we may expect a certain degree of ionization. We are investigating this aspect of the problem

* Ganesan and Venkateswaran, Ind. Journ. Phys. v. p. 195 (1929).

† Rao, Proc. Roy. Soc. A, cxxvii. p. 279 (1930).

and also studying the spectra of other nitrates, which will form the subject of a separate communication. Comparing this spectrum with that of amyl alcohol, we find the common frequencies 520, 1458, and 2880-2982.

TABLE VI.
Acetyl chloride, CH_3COCl .

Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference Δν.				
Wave-length in vacuum.	Inten- sity.							
5025.7	(1)	19897	4916.1 20336 cm. ⁻¹	439				
4998.9	(1)	20004	4358.3 (22938 cm. ⁻¹)	2934				
4731.7	(2)	21134	„	1804				
4648.4	(0)	21513	„	1425				
4632.9	(0)	21585	„	1353				
4609.4	(0)	21695	„	1243				
4593.9	(4)	21768	4046.6 (24705 cm. ⁻¹)	2937				
4475.3	(4)	22345	22938	593				
4443.7	(5)	22504	„	434				
4428.7	(1)	22580	„	358				
4293.5	(0)	23291	24705	1414				
4277.7	(1)	23377	22938	-439				
4249.0	(0)	23535	„	-597				
4235.4	(0)	23611	24705	1094?				
4211.4	(0)	23745	4108.9 (24337 cm. ⁻¹)	592				
4179.8	(0)	23925	4077.6 (24510 cm. ⁻¹)	585				
4147.2	(4)	24113	24705	592				
4121.2	(4)	24265	„	440				
4094.5	(1)	24423	3654.8 (27354 cm. ⁻¹)	2931				
4090.4	(1)	24447	3650.1 (27389 cm. ⁻¹)	2942				
Δν...	358	438	592	1243	1353	1420	1804	2936
λ(μ)...	27.9	22.8	16.9	8.04	7.39	7.04	5.54	3.40

Allyl Isothiocyanate.—The band at 3.5μ is here resolved into two components, 3.51μ and 3.42μ , corresponding to $\Delta\nu$ 2846 and $\Delta\nu$ 2920 respectively. Besides these, the most

prominent shifts are 710 and 1650. The new shift, 2085, which is diffuse, is characteristic of this liquid and may be

TABLE VII.
Benzoyl chloride, C_6H_5COCl .

Modified lines.		Wave-number cm. ⁻¹ .	Exciting line of mercury arc.	Wave-number difference $\Delta\nu$.
Wave-length in vacuum.	Inten- sity.			
5036.3	(0)	19855	4358.3 (22938 cm. ⁻¹)	3083
4726.0	(2)	21159	,,	1779
4716.3	(1)	21293	,,	1735
4687.1	(4)	21335	,,	1603
4623.8	(0)	21627	4046.6 (24705 cm. ⁻¹)	3078
4601.5	(2)	21732	22938	1206
4595.1	(2)	21762	,,	1176
4559.6	(4)	21932	,,	1006
4492.0	(1)	22262	,,	676
4480.8	(1)	22317	,,	621
4458.9	(1)	22427	,,	511
4440.9	(1)	22523	,,	415
4421.3	(1)	22618	,,	320
4327.1	(1)	23110	24705	1595
4301.8	(0)	23246	22938	-308
4284.3	(0)	23341	,,	-403
4266.7	(0)	23437	,,	-499
4250.8	(0)	23525	24705	1180
4219.6	(1)	23698	,,	1007
$\Delta\nu$	320 415 511 621 676 1006 1178 1206 1600 1735 1779 3080			
$\lambda(\mu)$	31.2 24.1 19.6 16.1 14.8 9.94 8.49 8.29 6.25 5.76 5.62 3.25			
* Benzaldehyde $\Delta\nu$...	 617 ... 1000 1168 1205 1598 1701 ... 3068			
† Benzene $\Delta\nu$...	 605 ... 991 1176 ... 1592 3061			

* Venkateswaran and Bhagavantam, Proc. Roy. Soc. A, cxxviii, p. 252 (1930).

† Ganesan and Venkateswaran, *loc. cit.*

attributed to N : C : S. This shift is also strong in phenyl mustard oil ‡ (C_6H_5NCS), where it has the value 2089. Comparing these two spectra, we find that allyl isothiocyanate

‡ Pal and Sen Gupta, Ind. Journ. Phys. v, p. 28 (1930).

shows all the characteristics of the aliphatic compounds, while phenyl thiocyanate shows the characteristics of the Benzene compounds.

Ethyl Oxalate.—The strong Raman frequencies in the spectrum of this compound are 866, 1454, 1761, and 2960. The last of these frequencies is due to the aliphatic C—H oscillation, and though it appears as a broad band it can be distinctly made out to be composed of two bands corresponding to 2980 and 2940. This frequency is nearly twice the other prominent shift, 1454. Likewise, the two shifts corresponding to 5.68μ and 11.6μ are also in this ratio.

Acetyl Chloride.—The very prominent frequencies here are 434, 592, and 2936. The first two are so strong that there appear corresponding anti-Stokes's lines, and also they are excited by the comparatively low intensity lines in the mercury arc as $\lambda 4916$ and the companions of $\lambda 4046$. The 3.4μ band is in this liquid quite sharp and single, unlike in other aliphatic compounds.

Benzoyl Chloride *.—The spectrum of this liquid is rich in lines and many small shifts corresponding to infra-red absorption wave-lengths greater than 15μ are observed, some of them giving anti-Stokes's lines also. The conspicuous frequency differences are 1006, 1603, and the two pairs of close doublets 1176, 1206 and 1735, 1779. There seems to be no relation between the spectrum of this liquid and that of acetyl chloride. Comparing the scattered spectrum of this liquid with that of benzene, we find that the 991 frequency of benzene is increased to 1006 and is equally prominent. The frequency 1592, which is faint in benzene, is very strong here. This spectrum bears a close resemblance to the spectrum of benzaldehyde †, the chief difference being that here, instead of the aldehyde shift 1701, we have the increased double shifts 1735 and 1779, which is probably the effect of replacing H with Cl. In acetyl chloride this takes the value 1804, and is also very prominent.

A very interesting feature in the scattering of this substance is the appearance of the spectrum taken with and without the quinine sulphate filter. Without the filter the Raman lines are completely absent, and we get a fluorescent

* Dadieu and Kohlrausch, *Monatsb.* liii. & liv. p. 282 (1929).

† Bhagavantam and Venkateswaran, *Proc. Roy. Soc. A*, cxxviii. p. 252 (1930).

spectrum from $\lambda 4500$ – $\lambda 5200$ and also a definite fluorescent band between $\lambda 5500$ and $\lambda 5700$. With the filter the fluorescence is absent, and the Raman lines come out very strong. (Plate XVI. *c, d.*)

Physics Laboratory,
College of Science, Nagpur.
April 18, 1931.

LXXX. *Note on the Paper of D. S. Kothari on the Limiting Density of Matter* *. By WILHELM ANDERSON, *Dr. phil. nat. (Tartu-Dorpat)* †.

MR. D. S. KOTHARI says: "It is obvious that ρ could not increase above a certain maximum value ρ_0 . The order of ρ_0 may be comparable to 10^{13} gm./cm.³, for n could be of the order of 10^{39} " Other scientists, too, have expressed a similar opinion ‡, and I also shared the same view formerly. Later on, however, I came to the conclusion that such a view would be difficult to reconcile with the theory of relativity, as we shall see presently.

The velocity of sound in a fluid is

$$v = \sqrt{\frac{d\rho}{d\rho}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and this equation, judging by its derivation, must be valid for any velocity, even for $v=c$. If we define the coefficient of compressibility by

$$\beta = \frac{1}{\rho} \frac{d\rho}{d\rho}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we obtain from (1) and (2)

$$\beta = \frac{1}{\rho v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since according to the theory of relativity $v \leq c$, we obtain from (3)

$$\beta = \frac{1}{\rho c^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As long as ρ is a finite quantity, the coefficient of compressibility β must remain finite too, *i. e.*, it is possible to

* D. S. Kothari, *Phil. Mag.* (7) xi. p. 1130 (1931).

† Communicated by the Author.

‡ G. I. Pokrowski, *Zeits. f. Phys.* xlix. p. 588 (1928); Seitarô Suzuki, *Phys. Zeitschr.* xxxi. p. 618 (1930).

compress the fluid ever more and more. In other words, there is no upper limit of density of matter. From the same reason the electrons and the protons too must be compressible*.

In the case of black radiation we have $p = \frac{\rho c^2}{3}$, and, consequently, $\frac{d\rho}{dp} = \frac{3}{c^2}$. This value, introduced in (2), gives $\beta = \frac{3}{\rho c^2}$. The value of this coefficient of compressibility is, then, three times greater than the limit value.

The impossibility of an upper limit of density is also capable of the following proof. If ρ_0 were the upper limit of density, we could bring into collision two bodies having this density and moving with the velocity v . At the moment of the collision the kinetic energy is transformed into potential energy, which, like any other kind of energy, has a certain mass. Thus at this moment the density would be no more ρ_0 , but $\rho_0 + \frac{\rho_0 v^2}{2c^2}$. Consequently ρ_0 is not the upper limit of density.

Tartu-Dorpat (Estonia),
Mühlenstrasse 30, Wohnung 2.

LXXXI. *The Effect of Low Temperatures on the Ultra-violet Transmission Band of Silver.* By Prof. J. C. McLENNAN, F.R.S., C. E. SMITH, M.A., and J. O. WILHELM, M.A., University of Toronto †.

[Plate XVII.]

ABSTRACT.

THE ultra-violet transmission band of silver was photographed at the temperatures of liquid air, liquid hydrogen,

* W. Anderson, *Zeits. f. Phys.* lvi. p. 855 (1929). Between the parts of one and the same electron there exists a strong electrostatic repulsion and a very weak Newtonian attraction. On compressing the electron its charge remains unchanged, whereas its mass is increased. Therefore the Newtonian attraction will increase at a greater rate than the electrostatic repulsion, until the two forces will finally equal each other. But then the electron would offer no more resistance to further compression: it would be possible without any further expenditure of work to compress the electron into a mathematical point and make it disappear completely. Thus the law of preservation of matter and energy would lose its validity under such extreme conditions. I leave, however, the question undecided whether so far-extending consequences are admissible in actual reality.

† Communicated by the Authors.

and liquid helium, and by means of microphotometer traces the positions of maximum intensity were obtained for these temperatures.

The mean frequency of the transmitted band was found to be approximately inversely proportional to the absolute temperature for the temperatures considered.

Introduction.

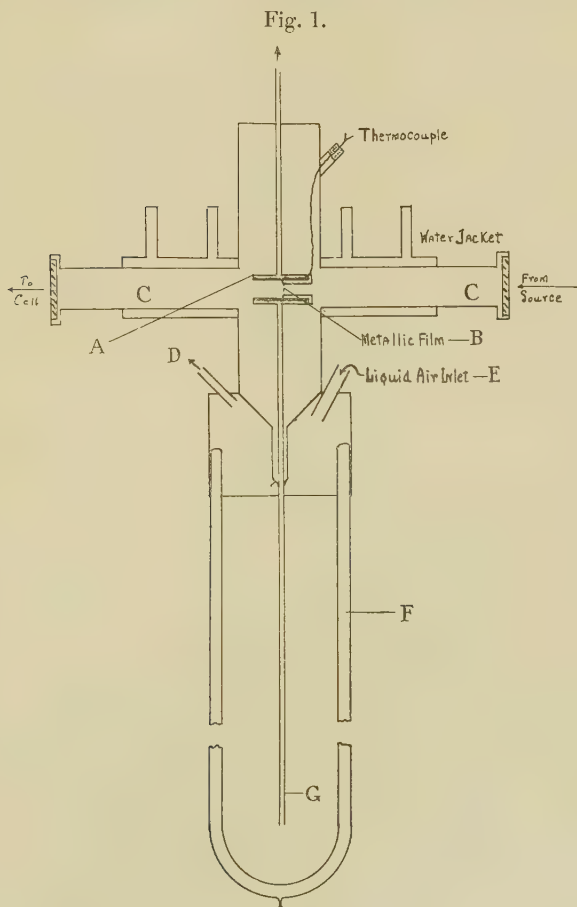
IT is well known that a study of the optical constants of silver reveals a discontinuity in the reflecting power in the ultra-violet. Stokes⁽¹⁾ showed that in the region of λ 3200 Å. the reflexion sinks in a short space almost to zero, while the transmission, as shown by Cornu⁽²⁾, attains a maximum in this region. While no marked change with temperature has been found in the optical constants of gold and platinum^{(3) (4)}, or molten bismuth, lead, tin, and Wood's alloy⁽⁶⁾, Ebeling⁽⁶⁾ was able to show a slight movement towards the red of the reflexion minimum of silver as the temperature was raised. An attempt to measure the absolute change in spectral position of the reflexion minimum was made by M. de Selincourt⁽⁷⁾, who worked between the temperatures of 100° C. and -183° C. He photographed the reflected light from a polished silver surface and measured the blackness of the plates by means of a photo-electric cell. He concluded that the phenomenon was due to the free electrons of the metal, which moved in sympathy with the heat vibrations of the atoms, and were controlled by the atoms themselves.

Owing to the fact that large inconsistencies may arise in results obtained in the use of polished surfaces due to their ageing, oxidation, and different methods of preparation, it was decided to study in the present investigation the transmitted rather than the reflected light. It should be stated here that a qualitative study of the breadth and position of the transmission band between the temperatures 254° C. to -180° C. was carried out by Lord Rayleigh⁽⁸⁾, and he was able to show very clearly a shift of the transmitted band towards the red as the temperature rose.

It was in order to discover whether there was any abnormal change in the spectral position of the band as the lowest temperatures attainable were reached that this investigation was carried out.

Apparatus.

Two forms of apparatus were used in the research. The first of these is shown diagrammatically in fig. 1. It consisted essentially of a hollow cylinder A, which was



connected by a thin German-silver tube G to a flask F containing liquid air or one of the other refrigerating liquids used. The inside of the cylinder A was provided with a thread into which could be screwed a small brass tube, across one end of which was supported the film to be studied. The tube A was enclosed by a jacket of thin German silver, having two arms C terminating in quartz windows. These arms were

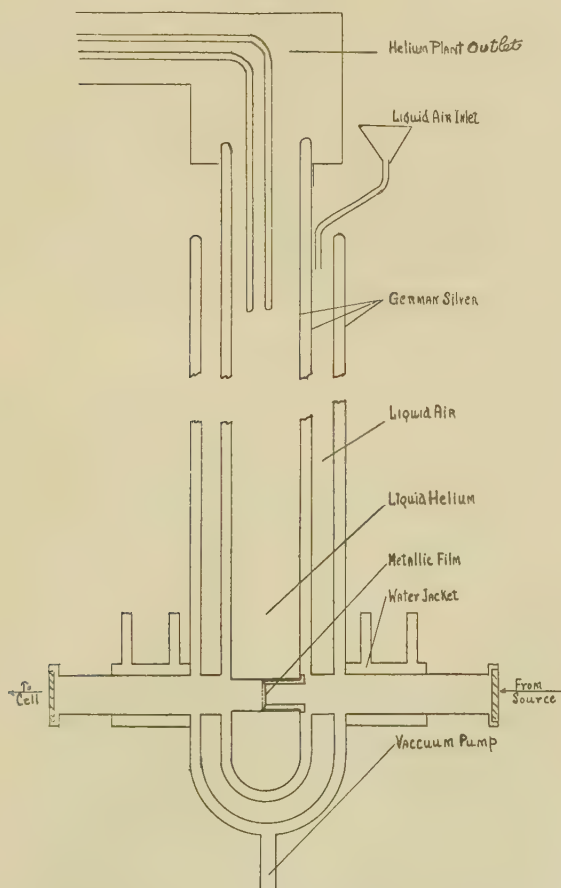
surrounded by water-jackets, so that by circulating water at room temperature through them during the experiment the windows were kept from fogging. The jacket was made to fit tightly over the mouth of the vacuum flask F and was secured during the experiment with rubber tape. The opening D was connected by a rubber tube with a pressure gauge. When liquid air was used as the refrigerant it was poured in at E by means of a funnel until the flask was sufficiently full. This funnel was then removed, and the orifice closed. With a suitable adjustment of the pressure at D, liquid air was forced up the tube G and made to pass around the film-holder; thence it was allowed to escape into the air through the top of the tube. A thermocouple (as shown) served to indicate when the requisite temperature was attained.

When the apparatus was used with liquid hydrogen as the refrigerant, the inlet E was connected with the source of liquid hydrogen and the liquid was forced into F by means of pressure from a cylinder of the compressed gas. When sufficient liquid hydrogen had been transferred to F the inlet E was closed, and by means of compressed hydrogen applied at D the liquid was forced up around A and so up the German-silver tube, which in this case was connected by rubber tubing with hydrogen storage gasometers.

For experiments with liquid helium it was necessary to use a different form of apparatus; this is shown diagrammatically in fig. 2. It was made of thin German-silver sheet, worked into proper shape, and consisted of two vacuum flasks placed one within the other. These were connected, as shown, at the lower end by thin-walled tubing, the inner section of which was threaded to take a brass film-holder similar to the one used in the liquid air and liquid hydrogen experiments. The outer ends were carried out, as before, into two arms which were closed by quartz windows and surrounded by water-jackets. During the experiment the vacuum flasks were connected with a mercury-diffusion pump in order to maintain a suitable vacuum for the high thermal insulation necessary when dealing with such low temperatures. The inner flask was connected directly with the helium plant, and a window and inclined mirror were provided at the top to enable the helium to be seen in the flask. Liquid air was kept in the outer flask during the experiment. In this way it was found possible to keep liquid helium in a metal flask without undue ebullition. During the experiment the film-holder was surrounded by liquid helium for over an hour.

The silver film used was beaten silver leaf, obtained commercially. A leaf of this was shaken from the book in which it was packed and allowed to fall on the surface of a bowl of water, where it floated in an extended position. A perforated disk of sterling silver was then brought up

Fig. 2.



from underneath in such a way that the silver film adhered. It was found that if the perforations in the silver disk were made with a very fine needle-drill it was possible to secure, stretched over these small holes, portions of the film free from the many imperfections found to be present in the large sheet. Moreover, the small areas of film stretched

over these small apertures were found readily to survive the strains of contraction to which the film was subjected at the low temperatures.

Various sources of light were tried, but finally it was decided to use a carbon arc. This gives an almost continuous spectrum in the region under consideration, and, in addition, there were two cyanogen lines at $\lambda 3591 \text{ \AA}$. and $\lambda 3881 \text{ \AA}$. which were sufficiently close and of sufficient intensity to appear on the plates after an exposure suitable for obtaining the transmission band. Light from the source was focussed through the film on to the slit of a small quartz spectrograph, which was used to record the emergent light; Ilford soft gradation panchromatic plates were found most suitable. Microphotometer traces were taken of the plates thus obtained, and these again were magnified geometrically, so that the total magnification was about sixty times. The centre of the band was thus estimated and the absolute position obtained from comparison with the known spectrum of the copper arc.

Results.

Pl. XVII. shows the four photographs obtained at room temperature and at the temperatures of liquid air, liquid hydrogen, and liquid helium. The known cyanogen lines are marked in each case, and also the positions of the centres of the transmission band, as estimated from the microphotometer traces shown in fig. 3. The characteristic wavelengths are given in the following table:—

Temperature	20° C.	−182° C.	−251° C.	−269° C.
Wave-length	3243 Å.	3212 Å.	3200 Å.	3198 Å.

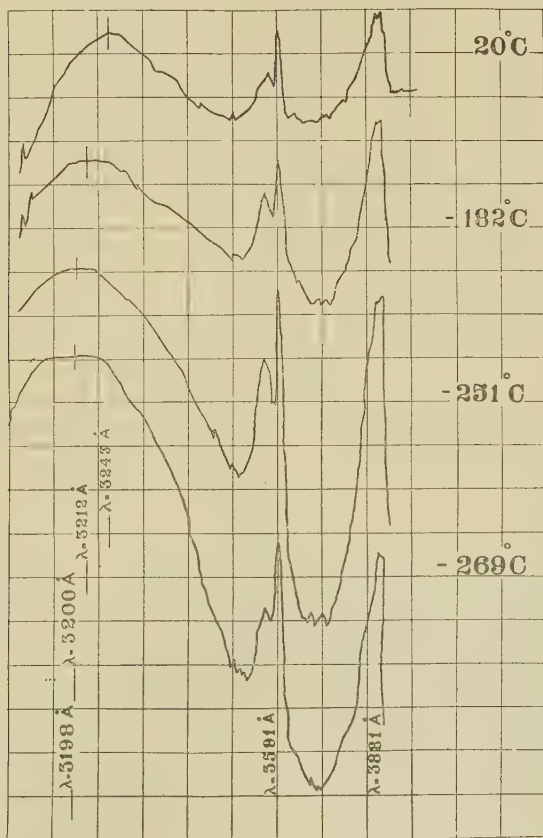
From the numbers given in the table it will be seen that the displacement of the transmission band, already observed in the higher range of temperatures, steadily but slowly increased down to the temperature of liquid helium.

The thermal dilation of silver was recently determined by Keesom and Jansen at Leyden, who showed that, while the contraction down to about -180°C . preserved a linear relationship with the temperature, the contraction below that temperature was less than a linear relation would require. The errors involved in our use of the microphotometer and in our estimation of the centre of the band were greater than the variation of the dilatation curve of silver from a straight line relationship. It was therefore not possible to show that this variation had any effect on the shift of the band. Fig. 4 shows the relationship we observed

between the frequency of the light transmitted and the temperature. It will be seen that it is practically a linear relationship. No abnormal variation in the shift was observed down to the lowest temperature attainable.

Another interesting effect that we observed was that as the temperature of the silver film was lowered the intensity

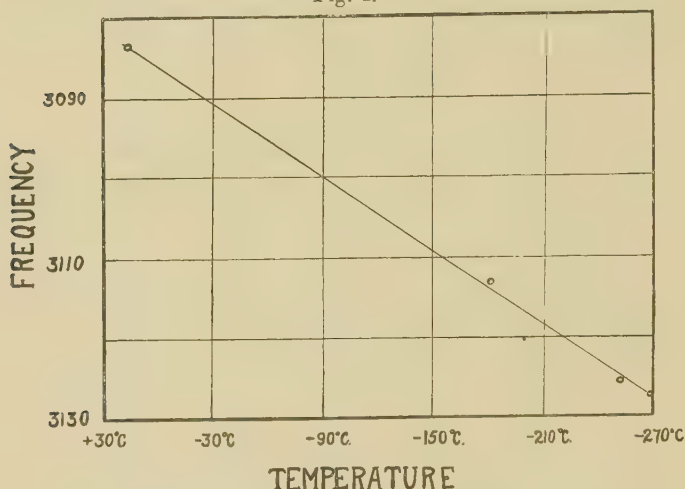
Fig. 3.



of the transmitted band became much greater, relative to that of the cyanogen lines. This effect, as fig. 3 shows, was so great that we had to use considerably shorter exposures at the lower temperatures. This increase in the intensity of the transmitted light with lowered temperature would seem to show that the resonance centres involved in the phenomenon diminished in number with decreasing temperature,

and the shift in the transmission band would appear to be due to a stiffening of the forces that bind such resonance centres as exist to their equilibrium positions. This

Fig. 4.



stiffening of the binding forces readily finds its explanation in the contraction undergone by the film with decrease in temperature.

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- (7) M. de Selincourt, *Proc. Roy. Soc.* cvii. p. 247 (1925).
- (8) Rayleigh, *Proc. Roy. Soc.* cxxviii. p. 807 (July 1930).

The Physical Laboratory,
University of Toronto.
Aug. 1, 1931.

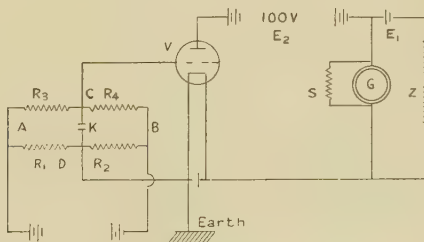
LXXXII. *On the Measurement of High Resistance by the Bridge Method.* By J. A. C. TEEGAN, M.Sc., A.Inst.P. *

THE ordinary bridge method of measuring resistance is unsuitable for resistances of a higher order than 10^6 ohms. The difficulty in such cases arises from the exceedingly small current in the bridge network and the

* Communicated by John J. Dowling, M.A., F.Inst.P.

resulting small current in the galvanometer branch. The method has been employed by Campbell* in his experiments on the resistance of xylol-alcohol mixtures, in which a sensitive quadrant electrometer (3000 divs. per volt.) replaces the ordinary galvanometer.

A method in which the electrometer is replaced by a robust galvanometer is described in this note, which has been found to give accurate and reliable results. The arrangement is indicated in the figure. It consists of a thermionic valve Mullard (I.L.F.) supplied with suitable H.T. and L. T. batteries. The normal anode current is compensated by that from the shunt circuit E_1 Z, E_1 being a single cell tapped off from the high-tension battery E_2 . The points C and D of the bridge usually connected to the galvanometer are joined to the grid and filament of the valve, so that both are initially earthed when the key K is closed, the galvanometer being reduced to zero by adjusting the



resistance Z . The arms of the bridge (R_1 and R_2) consist of the high resistances under comparison, the other arms (R_3 and R_4) being resistances taken from an ordinary box. In making a comparison of R_1 and R_2 the galvanometer is first reduced to zero with the key K closed. The key is then opened and R_1 and R_2 are adjusted until a balance is again obtained, giving the ratio R_1/R_2 in the usual manner. With the Mullard (I.L.F.) valve zero grid volts is a suitable working condition, and with 100 volts on the anode a voltage variation between C and D produces an anode current variation of approximately 1 milliampere. Using a Pye unipivot galvanometer, a voltage variation of $\cdot 001$ volt between C and D can be detected, so that R_1 and R_2 can be compared with an accuracy of 10 per cent. Higher degrees of accuracy can be obtained by using a more sensitive galvanometer, but trouble is then caused by the drifting of the zero, caused by unsteadiness in the batteries or variation in the emission of the valve.

* Campbell, Phil. Mag. p. 668 (1912); p. 1044 (1913).

842 *Measurement of High Resistance by the Bridge Method.*

The following tests of the method were made with the comparatively insensitive unipivot galvanometer, a voltage of 50 volts being applied to the bridge:—

(1) Comparison of a standard resistance of 250,000 ohm (r_1) and a Mullard megohm :

r_1	250,000 ohm.
r_3	2000 ohm.
r_4	1985 ohm.

Giving r_2 =resistance of the megohm = $\cdot 992 \times 10^6$ ohm.

(2) Comparison of the megohm with two resistances A and B of the order 10^7 ohm :

r_1	Resistance A.
r_2	Megohm.
r_3	10,740 ohm.
r_4	2000.

Resistance of A = $5\cdot 37 \Omega$.

r_1	Resistance B.
r_2	Megohm.
r_3	9440 ohm.
r_4	2000 ohm.

Resistance of B = $4\cdot 72 \Omega$.

Ratio—resistance A : resistance B = $1\cdot 138 : 1$.

(3) Direct comparison of the resistances A and B :

r_1	Resistance A.
r_2	Resistance B.
r_3	10,000 ohm.
r_4	8875 ohm.

Ratio—resistance A : resistance B = $1\cdot 125 : 1$.

(4) Measurement of a xylol-alcohol resistance contained in a sealed tube 50 cm. long, and $\cdot 2$ cm. radius, by comparison with the standard resistance of $2\cdot 1 \times 10^7$ ohm :

r_1	Resistance $2\cdot 1 \times 10^7$ ohm.
r_2	Xylol-alcohol resistance.
r_3	751 ohm.
r_4	10,000 ohm.

Resistance of xylol-alcohol = $2\cdot 79 \times 10^8$ ohm.

The mixture was made up from ordinary absolute alcohol (1 part) and commercial xylol (5 parts), and the tube was fitted with platinum electrodes, its outer surface being coated with shellac and earth connected. The specific resistance of the mixture came out as $\cdot 70 \times 10^7$ ohm, which is somewhat

lower than the value obtained by Campbell. The lower result is probably due to the fact that neither the alcohol nor xylol were so completely dried as in Campbell's experiment.

Gresham's School, Norfolk.

May 9th, 1931.

LXXXIII. *Electrical Oscillations of very short Wave-length.*

By E. W. B. GILL, *B.Sc., M.A., Fellow of Merton College, Oxford* *.

1. **I**N 1919 Barkhausen and Kurz † discovered that an ordinary 3-electrode valve, whose anode and filament were at approximately the same potential and the grid kept charged positively, was capable of maintaining continuous oscillations of very short wave-lengths of the order of a metre.

The wave-lengths depended on the natural periods of the external circuits, but the fact that the oscillations rarely occurred on the fundamental wave-length of these circuits, but on one of the other possible modes of oscillation, indicated that the regenerative action of the valve was most effective for particular wave-lengths. The action of the valve when connected in this way is not the same as in more ordinary circuits, where the fundamental oscillation is practically always maintained by the regenerative action of the valve, and the valve is equally efficient over a large range of wave-lengths. J. H. Morrell and the author ‡ came to the conclusion that if V is the potential maintained between the grid and other electrodes the oscillations produced would be strongest if the external circuit was tuned to a wave-length λ such that $\lambda^2 V$ is equal to a constant depending only on the dimensions of the valve. The experiments to be described show that this result is only partially true; the dimensions of the valve then used were unsuitable for showing what happens in the more general case.

2. The arrangement of the circuit now used is shown in fig. 1.

The oscillatory circuit consisted of two Lecher wires LL, each 616 cm. in length, attached to the grid and anode terminals of the valve. These wires, 6.5 cm. apart, were of tinned copper no. 18 gauge.

* Communicated by Prof. J. S. Townsend, F.R.S.

† *Phys. Zeits.* Jan. 1920.

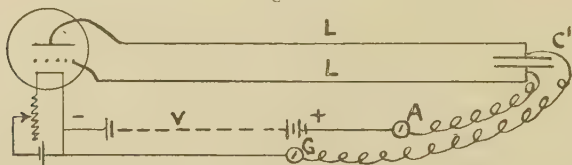
‡ *Phil. Mag.*, July 1922, p. 161.

The wires were also joined through the condenser C, from which the anode lead went to the negative end of the filament through a microammeter G, and the grid lead through a milliammeter A to the positive terminal of a battery of accumulators, the negative terminal of which was also joined to the filament.

The oscillatory circuit comprised the capacity formed by the grid and anode, the distributed inductance and capacity of the valve leads inside the valve, and the distributed inductance and capacity of the wires L. The capacity C was large and for short-wave oscillations could be regarded as a short circuit.

The wave-length of the fundamental oscillation of this circuit was of the order of 30 metres, and among its other modes of oscillation were wave-lengths of 576 cm., 400 cm., 304 cm., and 248 cm. The condenser C was a potential node, and for all the oscillations except the fundamental there were also potential nodes half a wave-length apart along the wires LL. Thus the 576 cm. wave had 2 nodes,

Fig. 1.



the 400 cm. 3 nodes, and so on. There are generally also nodes in the valve leads inside the valve. The study of the conditions necessary to produce oscillations of the above four wave-lengths was sufficient to establish certain laws, and the experiments were made on these wave-lengths only. The wave-lengths were measured experimentally. The existence of oscillations was indicated by a large deflexion of the microammeter G. The anode being at the same potential as the negative end of the filament, no current can normally reach it from the filament except a very minute one due to the faster electrons emitted from the hot filament. If G shows an appreciable current it indicates that oscillations are occurring in which for alternate half-cycles the anode is positive in potential to the filament, since the latter is attached to a potential node at C. In these half-cycles the anode receives current. It is also clear that the deflexion of G gives a measure of the amplitude of the oscillations.

Further evidence for the galvanometer reading indicating the existence of oscillations is that in general, if either of the wires LL is touched, this reading of G sinks to a low

value. There are, however, a few points of the wires which can be touched without affecting the current in G, and these points are the potential nodes. This affords a rapid and simple method of measuring the wave-lengths. The blade of a knife was run along one of the wires, the nodes found, and thus the half-wave-length measured.

The valve used had a cylindrical anode and grid coaxial with a straight filament. The grid was 5 mm. and the anode 25 mm. in diameter. The anode was unusually large compared to the grid, and the valve was selected for this reason. It had been used on several previous investigations, and its vacuum was not so good as that of a modern valve.

3. In the first set of experiments the filament was heated to considerably below its maximum temperature, and the potential V of the grid raised by steps of approximately 2 volts, starting from zero. It was found that the current shown by G rose to a maximum when V was 24 volts, and fell again for a further increase of V. The above described tests along the wires showed that when V was 24 volts oscillations were occurring on a wave-length of 576 cm. Further increases in V produced no more oscillations unless the temperature of the filament was increased, in which case a wave of 400 cm. was produced with maximum amplitude when V was 50 volts. A further increase of temperature of the filament and higher value of V gave the 304 cm. wave most strongly with 91 volts, and, finally, the 248 cm. wave was got with 157 volts.

As the temperature of the filament, or, in other words, the emission from the filament, appeared to be of importance, the experiments were repeated, adjusting the filament-heating current in each case to give the maximum amplitude of oscillation. The corresponding grid-currents were given by the milliammeter A. The final results are given in Table I., λ being the wave-length in metres, i the grid-current giving maximum oscillation in milliamperes.

The fourth column shows that $\lambda^2 V$ is approximately constant, and the fifth that i is proportional to $V^{3/2}$.

The agreement for $V=157$ is not good. This is due to the valve not having a sufficiently good vacuum, and will be discussed in sect. 5.

A further set of experiments was then made with the grid voltage kept constant and the filament temperature varied.

With V kept at 24 volts the gradual increase of filament emission first excited the wave-length of 576 cm., whose amplitude of oscillation reached a maximum when the grid-current reached .66 m.a., a further increase of filament-heating reduced this amplitude to zero, and then a fresh

oscillation, found to be the 400 cm. wave, was set up, which reached its maximum for a grid-current of 1.3 m.a. The same thing occurred with further heating, a grid-current of 2.06 m.a. giving a maximum amplitude of the oscillation of 304 cm. wave-length. This was the last wave-length of the four that could be obtained by increasing the filament temperature. Similar experiments with the grid at 50 volts showed that the strongest oscillation on 400 cm., 304 cm., and 248 cm. wave-lengths were obtained with grid-currents of 2.25, 4.0, and 6.4 m.a. respectively. These results are given in Table II.

TABLE I.

V.	λ .	i .	$\lambda^2 V$.	$V^{3/2}/i$.
24	5.76	.66	799	178
50	4.00	2.11	800	167
91	3.04	5.04	841	170
157	2.48	12.5	965	154

TABLE II.

V = 24.

i .	λ .	$\lambda^2 i$.
.66	5.76	21.8
1.3	4.00	20.8
2.06	3.04	19.2

V = 50.

2.25	4.00	36
4.0	3.04	37.2
6.4	2.48	38.6

The last columns show that, if V is fixed, $\lambda^2 i$ is practically constant.

It appears, therefore, that with the valve used a grid voltage V is capable of maintaining oscillations over a range of wave-lengths, and not, as was supposed, on one wave-length only. The wave-length most strongly maintained depends not only on V, but also on the grid-current.

When V is 24 volts the only wave-lengths below 576 cm. which the external circuits allowed were 400 cm., 304 cm., and smaller; it is clear that with suitable external circuits a value of the grid-current could be found which would maintain any wave-length, between 576 cm. and 304 cm. The actual lower limit is not known from these experiments, but it is between 246 cm. and 304 cm. The theory given later indicates that 576 cm. is practically the upper limit to the wave-length maintained.

The summary of the results in Tables I. and II. thus gives (for the wave-lengths most strongly regenerated) that the

wave-length λ depends on both the grid-volts V and the grid-current i , but that the possible wave-lengths are confined to a band. The long wave ends of the bands obey the law, $\lambda^2 V$ is constant, and the appropriate values of i for these are proportional to $V^{3/2}$ (Table I.).

In addition for all waves in the band given by a definite value of V the relation $\lambda^2 i$ is constant is obeyed (Table II.).

In general, therefore, for any values of i and V we must have $\frac{\lambda^2 i}{\sqrt{V}}$ is constant, which is more general than the old relation $\lambda^2 V$ is constant which applies only to the long wave limit.

4. Although this particular method of producing short-wave oscillations has been known for ten years, no really satisfactory theory has been given.

J. H. Morrell and the author put forward an approximate theory in 1922 based on energy considerations, and although the calculations based on the energy are still valid, the particular assumptions made that the number of electrons passing through the grid per second is always the same is not correct. An explanation often given is that the electrons leave the filament, pass through the grid, turn back at the surface of the plate, and, after again passing the grid, return close to the filament. If the stream of electrons is not uniform, but varies in density, whenever a dense group of these returning electrons gets near the filament, the filament emission is momentarily reduced, and this is supposed to result in alternate bursts of electrons moving across the valve.

This explanation, among other things, demands that the space between filament and grid is carrying its saturation current, as only in this case would electrons returning to the filament reduce the current leaving the filament.

The experiments with $V=24$ prove that oscillations commence long before the space between the filament and grid is saturated. The 576 cm. wave occurs when the grid-current is only .62 m.a., and further heating of the filament gave a grid-current of 2.06 m.a.

Another suggestion was that oscillations are only possible if the valve is not quite hard but contains a little gas. Actually the oscillations may be rather more powerful if the valve is slightly soft, but it is not a necessary condition for oscillation.

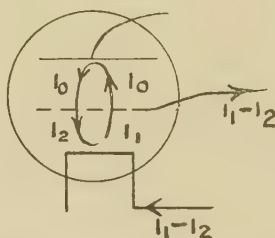
The theory to be developed is based on the assumption that oscillations are maintained when the space between the grid and anode is carrying its saturation current, *not* the space between filament and grid.

The scheme of currents before oscillations commence is shown in fig. 2.

A proportion of the electron stream leaving the filament is collected on the grid. The rest passes through the grid and comes to rest at the surface of the anode, and then returns to the grid, where a proportion are again collected. The rest move to the vicinity of the filament and then rejoin the outgoing stream. All electrons are finally caught on the grid, but they may have made several excursions before this happens. The net result is that at any instant in the space between the grid and filament there is an outward current i_1 and inward i_2 , and in the space between grid and anode outward and return currents i_0 .

The grid-current, which is equal to the current leaving the filament, is $i_1 - i_2$, and is the only current which can be measured directly.

Fig. 2.



I have in a previous paper* discussed in some detail the effect of the space-changes between anode and grid on the field there, and it was easy to see that the considerations in Langmuir's well-known results on the saturation current between a filament and coaxial cylinder apply equally to the currents in the space between anode and grid. It follows, then, that the maximum current i_0 which can flow in this space when the electrons just fail to reach the anode is proportional to $V^{3/2}$.

As remarked above, the current i_0 cannot be measured directly, but it may be assumed that it is proportional to the grid-current $i_1 - i_2$.

Table I. shows that the grid-currents for the maximum amplitudes of oscillation of longest wave-length are proportional to $V^{3/2}$, so that i_0 is also proportional to $V^{3/2}$, which suggests that this space is saturated.

Of course if the space between filament and grid were saturated the result would again be that i_0 was proportional to $V^{3/2}$, but as this space is certainly not saturated for the

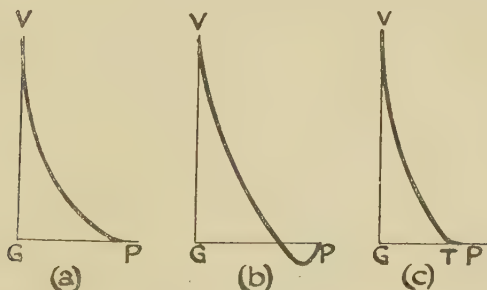
* E. W. B. Gill, *Phil. Mag.*, May 1925, pp. 998 & 999.

currents in Table I. the agreement with the $V^{3/2}$ law indicates very strongly that saturation has occurred in the only other possible space, *i. e.*, between grid and anode. In all that follows the grid and anode will be regarded as parallel planes, as the calculation for cylinders introduces considerable difficulties.

The effect of the negative charge on the electrons between the grid and anode is to reduce the electric force due to the fixed potential near the anode and increase it near the grid, and in the limiting case when the current is saturated the electric force at the anode is reduced to zero.

The potential distribution for this case is shown in fig. 3 (a), where ordinates represent potentials and abscissæ distances from the grid. GV is the potential of the grid at G and P is the anode whose potential is zero. The curve touches GP at P.

Fig. 3.



The space-charge is, of course, due to the charges on all the electrons in the space, whether moving towards or away from the anode.

If the above saturated potential distribution is disturbed, oscillations may be set up and maintained, as outlined in the following theory. When the saturation current i_0 is flowing electrons enter the space at a uniform rate, and, after turning at the anode, reach the grid-plane at the same uniform rate. Let T be the time an electron takes to go from the grid-plane to its turning point at the anode or *vice versa*.

Suppose now at time $t=0$ the system is slightly disturbed by suddenly putting a small positive charge on the anode. The electrons in the stream in the vicinity of the anode are at once attracted to the anode, the charge is neutralized, and the anode returns to zero potential. The sudden removal of the electrons at a point in the stream means that its uniformity is disturbed, and what may be termed a point of rarefaction travels along the return stream and arrives back

at the grid-plane at a time T after the loss of electrons to the plate.

During this interval of time T the space is no longer saturated. The question when this space next saturates requires a rather careful consideration of what factors determine the current i_0 which enters the space. It is here necessary to remember that, although the electric field in practically all the space can be regarded as that between parallel planes, this is not so very close to the grid, which is composed of parallel wires.

The electric field near the grid determines what proportion of the electrons from the filament side passes through it and what proportion is collected direct. This field, besides being produced by the fixed potentials, is also affected by the charges on the moving electrons, and by far the greatest effect is produced by those close to the grid. The rarefaction in the return stream has therefore practically no effect till it gets quite close to the grid, when the repulsive force of the electrons in the return stream is reduced and the flow of electrons into the space is therefore momentarily increased—in fact, what may be termed a compression enters. Up till this instant the rate of entry has been the normal one corresponding to current i_0 .

The situation in the space between grid and anode just before time T is therefore that a compression has just entered; in front of it is the normal stream up to the anode and back again, and at the head of it, just about to leave the space through the grid, is the rarefaction. But as soon as the rarefaction has passed out the space, owing to the compression, is “over saturated”. This possibility is discussed in a paper on “Space Charge Effects”*, where it is shown that when the compression gets near the anode the field at the anode is actually reversed with a potential distribution of fig. 3 (*b*).

In consequence the electrons near the anode are again collected on it and may be collected in such numbers that the compression in the stream is turned into a rarefaction.

It is evident that after this the process repeats itself indefinitely, the anode receiving negative charge at times $2T$, $4T$, etc., and resonance will therefore occur in an attached circuit, whose periodic time is also $2T$. The same argument applies if the number of electrons entering the space varies harmonically with the time and has a period $2T$. It is worth noticing that the electrons are forced on to the anode by the repulsion of those just behind, whose energy is derived from the high-

* E. W. B. Gill, *Phil. Mag.*, May 1928, p. 859.

tension battery, which is therefore ultimately the source of energy of the oscillations.

The theory thus far indicates that the oscillation which will be maintained with greatest amplitude has a period $2T$, where T is the time taken by an electron to move between the grid and anode. Still regarding the electrodes as parallel planes, it is easy to show if the potential between them is V that the time an electron takes to move across in the saturated field of fig. 3 (a) (for which Childs has shown that the potential is everywhere proportional to the distance from the anode raised to the power $\frac{4}{3}$) is exactly $\frac{3}{2}$ times the time to pass across if the potential is V and the force uniform.

If the distance from anode to grid is d cm. in the uniform field, the electric force is V/d , and the time the electron takes to cover the distance d is $d\sqrt{\frac{2m}{eV}}$, m and e being mass and charge of an electron. (The alternating potentials superposed on the fixed potentials are small enough to be neglected.)

Hence in the saturated field

$$T = \frac{3}{2}d\sqrt{\frac{2m}{eV}},$$

whence the periodic time of resonating oscillation

$$= 2T = 3d\sqrt{\frac{2m}{eV}}.$$

If λ is the wave-length of this oscillation in metres, putting in the values of the constants and measuring V in volts we get very approximately

$$\lambda = \frac{30d}{\sqrt{V}}$$

$$\text{or} \quad \lambda^2 V = 900d^2.$$

This agrees with the experiments, which show that $\lambda^2 V$ is constant when the space from anode to grid is carrying its saturation current.

For the valve used d was almost exactly 1 cm., giving the calculated value of the constant as 900, which, compared with the experimental value of about 800 in Table I., is as reasonable an agreement as could be expected with the assumption that the electrodes were parallel planes.

It remains to explain why the limiting wave-lengths obeying the above relation are not the only wave-lengths which can be excited. The maximum current which can pass between the anode at potential 0 and grid at potential V ,

if they are regarded as parallel planes distant d apart, is proportional to $\frac{V^{3/2}}{d^2}$.

There is, however, a possibility of a larger current flowing if the discharge contracts its dimensions, *i. e.*, if the electrons instead of penetrating just to the anode stop short at a distance d_1 from the grid. The potential distribution will then be as in fig. 3 (c), in which T represents the turning-point and the space from T to P is all at zero potential.

In such a case the maximum current which can flow is proportional to $\frac{V^{3/2}}{d_1^2}$ and is larger than that for distance d .

With such a distribution of potential oscillations will occur in exactly the same way as before.

The wave-lengths λ will now be proportional to $d_1/\sqrt{V}$, and if i_0 is the corresponding value of the current in the space, i_0 is proportional to $\frac{V^{3/2}}{d_1^2}$.

Whence

$$i_0 \text{ is proportional to } \frac{\sqrt{V}}{\lambda^2}$$

or $\frac{\lambda^2 i_0}{\sqrt{V}}$ should be constant.

That is to say, if i_0 is a constant fraction of the grid current i ,

$$\frac{\lambda^2 i}{\sqrt{V}} \text{ must be constant,}$$

which agrees with the final experimental result in sect. 3.

5. It appears therefore that oscillations first begin when the current from the filament passing the grid is just sufficient to saturate the space between the grid and anode with the electrons penetrating to the anode surface. These oscillations obey the $\lambda^2 V$ law, and are the longest waves generated with maximum efficiency. If more electrons are forced into the space the wave-length shortens, obeying the relation $\lambda^2 i/\sqrt{V}$ is constant, where i is the grid-current.

The limit to the size of the current which can be forced through the grid is fixed by the conditions on the filament side of the grid. When the filament emission reaches the value corresponding to the maximum current which can pass across the space from filament to grid it is evident that no more current can be forced through the grid, and the short-wave limit is thus reached when the filament grid-space is saturated.

With the dimensions of ordinary valves the current to saturate the filament grid-space is only a little more than that required to saturate the anode grid-space, and the possible wave-lengths regenerated are confined within narrow limits. This was the case in the original experiments with J. H. Morrell, the range being so small that it appeared to consist of only one wave-length. The special valve now used, in which the grid anode-space was much larger than the filament grid-space, gives a much larger range.

If in a valve the grid is nearer to the anode than to the filament the grid anode-space can never get the maximum current it is capable of carrying, and oscillations cannot occur. This has been confirmed experimentally.

If there is a small trace of gas in the valve the saturation of the anode grid-space is rendered more difficult owing to the positive ions produced by collision neutralizing the negative space-charge effect of the electrons.

This effect only becomes prominent at the higher voltages, as the ionization is then appreciable, and accounts for the disagreement between the results for $V=157$ and the others in Table I. With $V=157$ the anode-current was in the reverse direction before the oscillations began, indicating the collection of positive ions. When the oscillations began the anode received both positive and negative charge, the latter being in excess, and the deflexion was in the usual direction for an oscillation.

I am much indebted to Professor Townsend, in whose laboratory the experiments were made, for his assistance with this paper.

LXXXIV. *X-Ray Examination of Electroplated Chromium Coatings.* By W. A. WOOD, M.Sc., *Physics Department, National Physical Laboratory, Teddington, Middlesex* *.

[Plate XVIII.]

ABSTRACT.

1. The existence of hexagonal chromium is confirmed, and conditions for obtaining it are determined.

2. Chromium deposited electrolytically is found to give very broad X-ray diffraction lines. The breadth of the

* Communicated by Dr. G. W. C. Kaye.

lines is put down to the very finely divided nature of the deposit, and the grain size is estimated. It is found to vary in a regular way with the conditions of electro-deposition.

3. An anomalous distribution of intensity in the X-ray spectra is observed. It is explained on the assumption of the presence of a majority of grains of a particular shape.

4. This last effect is found to be associated with the brilliant type of deposit.

Introduction.

IN recent years electroplating by means of chromium has been the subject of extensive application. The value and use of the chromium coating depend largely upon the extreme hardness of the metal and upon the possibility of securing it with a brilliant lustre which will withstand, with comparative success, the action of severe corrosive agents. These properties vary greatly, however, with the conditions under which the deposit is obtained. For example, discussing a paper by E. A. Ollard on chromium-plating W. E. Harris⁽¹⁾ states that at a given current density by increasing the temperature of the plating bath one obtains, in order, a matt deposit ranging in colour from dark to light grey, a highly brilliant deposit even after hours of deposition, and a smooth but scanty deposit of bluish tinge. Also, R. Piersol⁽²⁾ found that the hardness of a deposit, measured by abrasion tests, may vary by as much as forty-three times as the current density is changed at a given temperature. It becomes a matter of some interest therefore to see what information can be added to the findings of metallurgical investigations by examination in the light of X-rays. The problems peculiarly amenable to X-ray analysis are those connected with the determination of grain size, especially when the particles are so small as to be beyond the limit of microscopic resolution, with the possible presence of small amounts of crystalline impurities, with preferential orientation of a particular crystallographic axis of the grains, with lattice distortion, and with the formation of allotropic modifications of the metal. Attention is paid to these points in the paper; also an example is found of a case, of importance to the physicist, where the relative intensities of an X-ray spectrum may vary without changes in the atomic structure of the diffracting material.

Hexagonal Chromium

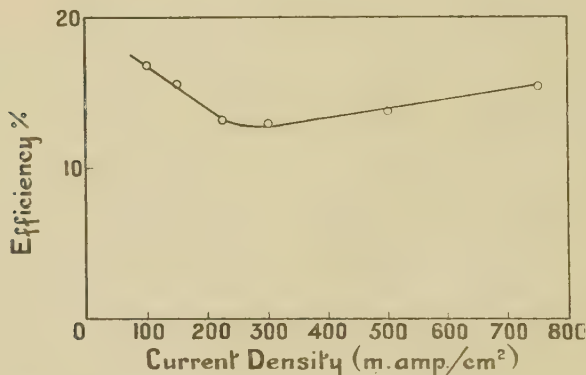
A certain amount of controversy has arisen on the question as to whether, in addition to the normal body-centred cubic form of chromium, a hexagonal modification can be obtained by electro-deposition, with consequent alteration of the properties of the substance. A. J. Bradley and E. A. Ollard⁽³⁾ found that chromium, prepared by a method not described in their notice, could consist of a mixture of these two allotropes. The result has been contradicted by C. S. Smith⁽⁴⁾ and also by F. Sillers⁽⁵⁾. In a discussion of a paper by the latter a contribution sent by Ollard stated that Sillers would have obtained the hexagonal form with the particular type of chromic acid bath used if he had worked it at a higher current density and lower temperature. Sillers, following these recommendations, found, however, no trace of the hexagonal allotrope. Whilst the present work was in progress K. Sasaki and S. Sekito⁽⁶⁾ obtained the latter, using a chromic sulphate bath, and they state that the conditions for its formation are those prescribed by Ollard for the chromic acid bath—contrary to the experimental evidence of Sillers.

In the following work deposits of chromium were made on chemically cleaned copper wire first by the use of a bath composed of 25 per cent. of pure chromic anhydride, Cr_2O_3 , and $\frac{1}{4}$ per cent. of sulphuric acid. This is presumably similar to that used by Sillers. Varying current densities were employed at temperatures ranging from 13°C . to 70°C . A lead anode was used. The thickness of the deposits varied up to 0.38 mm. and the surfaces from the dark grey matt to the highly polished type. The coated wires were placed at the centre of a circular camera, and a diffraction photograph obtained by the use of chromium radiation. The risk of affecting the deposits by separating them from the base metal was thus obviated. A second type of plating bath was also used containing $\frac{1}{4}$ per cent. of sulphuric acid and 50 per cent. of chromic acid reduced by the addition of a little sugar.

With the first bath no trace of the hexagonal form was found in any of the deposits, thus confirming the conclusions of Sillers. On the other hand, using the second type of bath the hexagonal allotrope mixed with the cubic was definitely obtained, the shape and size of the unit cell agreeing with that described by Bradley and Ollard (*loc. cit.*). The proportion of hexagonal chromium present varied with the current density and temperature of the bath. It ceased to form as the temperature approached 30°C . At room

temperature a current density of 100 milliamps. per sq. cm. gave a deposit with no trace of the hexagonal variety. It appeared first at 150 milliamps per sq. cm., and increased in proportion as the current was increased to 220 milliamps. per sq. cm., and then as the current was further increased to 750 milliamps. per sq. cm. began slightly to diminish in amount compared with the quantity present of the cubic type. The efficiency of the bath was determined for each deposit. It was taken as being equal to the weight of deposited chromium divided by the weight which should have been deposited according to Faraday's law; the valency of chromium was assumed to be 3 for purpose of calculation. A graph typifying the change of efficiency with current density at room temperature is given in fig. 1. The point

Fig. 1.



of interest is that the efficiency was highest when the deposit was wholly cubic and lowest when the proportion of hexagonal present—at 220 milliamps per sq. cm.—was a maximum. The slight rise of efficiency from 220 to 750 milliamps. per sq. cm. corresponds with the observation from the photographs that the proportion of hexagonal decreased slightly with increase of current in that range. With only cubic material present the efficiency changes with current in quite a different way (*vide* Tables).

One must conclude that the confusion of evidence on the existence of the hexagonal allotrope arises from the fact that, in addition to using the correct conditions of current and temperature, one must use a bath modified in the same way as that described. This would explain the results of Sillers and of Smith, who apparently did not. The case of a chromic sulphate bath has been given by Sasaki and Sekito

(*loc. cit.*), and is not dealt with here. It should be noted, however, that the contradictory result of Smith using chromic sulphate would follow from his use of a bath saturated with hydroxide. The former suppressed the formation of hydroxides and salts, the acidity of the bath being again apparently the important factor.

Lattice Distortion.

The interference lines obtained by photographing the deposits were in every case remarkably diffuse. The breadth of the lines varied within wide limits for deposits differently obtained. It appears reasonable to anticipate that the variations should be related in some degree to the deposits which possess different properties. The explanation of the changes in breadth may be based either on the assumption of distorted lattices or on the presence of particles of size less than about 10^{-6} cm. The possibility of distinguishing to which cause the effect is to be assigned depends on what the type of distortion is likely to be. A diffraction line due to the distorted lattice of one small crystal is not necessarily broadened by distortion. In some cases, as it is hoped to show elsewhere, it may actually be sharpened; but when the spacings of a lattice are partially increased, as one would expect, by the distortion due to the presence of a strange atom in solution, then the angle of diffraction for those spacings is decreased, and *vice versa*. Consequently the angles of diffraction for a mixture of small crystals distorted by different amounts are spread over a definite range depending on the maximum distortion which occurs, and the interference lines are correspondingly diffused. It is reasonable to expect, however, that the distortion is unidirectional: it tends either to increase a set of spacings or to decrease them, but not to do both. Therefore distortion should result in a shift of the position of maximum intensity of a diffuse line when compared with the position of the sharp line of the normal lattice. Such an alteration was searched for in the cases under consideration, but not found. The normal spectrum was obtained by heating one of the chromium coatings, which gave a very diffuse line to 700°C . for two hours *in vacuo*. Photographs of this deposit now gave sharp lines, the (211) line showing a well separated α , α' doublet, and this photograph was taken to represent undistorted chromium with large crystals. Comparison of this photograph with the others revealed no spacing changes; the diffuse lines broaden symmetrically about the position of the normal sharp lines. This is illustrated by figs. 1 and 2 in Pl. XVIII. The broadening is therefore assumed to be

due to the very finely divided nature of the grains composing electroplated chromium.

Variation of Grain Size with Current and Temperature.

The chromium plating bath used as standard contained 25 per cent. of Cr_2O_3 and $\frac{1}{4}$ per cent. of sulphuric acid. A piece of lead sheet, bent cylindrically, was used as anode, and was well cleaned before each experiment. A length of copper wire of 0.89 mm. diameter served to take the deposits. The same type of wire was used throughout. Each deposit was photographed without removing it from the wire in a cylindrical camera, of diameter 10.40 cm., and the photographs were developed and fixed under standard conditions of time and temperature. The thickness of the deposits was determined by weighing known lengths of the plated wire and checked by measurement with a micrometer gauge. The deposits were obtained with the bath at room temperature, 30° C., 50° C., and 70° C. At each temperature current densities of 50, 100, 150, 200, 250, and 750 milliamps. per sq. cm. were employed. The breadths of the diffraction lines for each deposit were measured by the aid of a Moll microphotometer, the procedure adopted being that previously described⁽⁷⁾ by the author, and therefore not repeated here. Measurements were based on the (211) line which, occurring at 77° 2' with the chromium radiation, showed most markedly the changes in breadth. This line is a doublet, so that it is necessary to correct for the presence of the α' component. This is done simply by a method described fully by R. Brill⁽⁸⁾. If B is the measured half-breadth and b the corrected value, then it can be shown that

$$b = \frac{B}{2} \left\{ 1 + \sqrt{1 - \frac{4\delta}{3B}} \right\},$$

where δ is the separation of the doublet. A further correction is required for absorption before the Laue equations connecting line breadth with grain size can be applied. This involves the division of the breadth by $\sin^2 \theta$, where θ is the diffracting angle⁽⁸⁾. A fuller correction given recently by Brill⁽⁹⁾ is not used because it does not greatly affect the lines when the diffraction angle is large. Moreover, the extra degree of accuracy is hardly warranted in view of other simplifying assumptions made in Laue's solution of the mathematical problem.

The results of the measurements of the half-breadth of the (211) line of the different deposits are described in Tables I., II., and III. In column 1 is given the half-breadth, in centimetres, after correcting for the presence of

the α' component; in column 2 is given the current density in milliamps. per sq. cm. used to obtain the deposit; in column 3 the estimated efficiency, in column 4 a description of the type of the deposit, and in column 5 the grain-size

TABLE I. 30° C.

Breadth <i>b</i> .	Current density.	Efficiency.	Description.	Grain-size.
cm.	milliamp/cm. ² .	per cent.		cm.
*0.73	50	8.1	Bright, smooth.	7.5×10^{-7}
0.62	100	9.0	Grey, metallic.	9.1×10^{-7}
0.55	150	10.2	Grey, metallic.	10.3×10^{-7}
0.37	200	10.0	Dull grey matt.	15.2×10^{-7}
0.30	250	14.2	Dark grey matt.	18.8×10^{-7}
0.34	750	20.1	Dark grey matt.	16.5×10^{-7}

TABLE II. 50° C.

Breadth <i>b</i> .	Current density.	Efficiency.	Description.	Grain-size.
cm.	milliamp/cm. ² .	per cent.		cm.
*0.55	50	5.3	Bright, smooth.	10.3×10^{-7}
*0.47	100	6.0	Bright, smooth.	11.9×10^{-7}
*0.43	150	5.5	Bright, smooth.	13.1×10^{-7}
*0.42	200	5.5	Bright, smooth.	13.5×10^{-7}
*0.40	250	5.9	Bright.	14.0×10^{-7}
*0.44	750	13.0	Bright.	13.0×10^{-7}

TABLE III. 70° C.

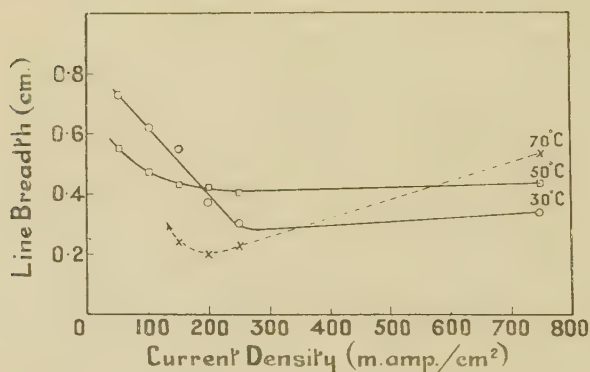
Breadth <i>b</i> .	Current density.	Efficiency.	Description.	Grain-size.
cm.	milliamp/cm. ² .	per cent.		cm.
Scanty deposit.	50	Small.	Scanty.	—
Very broad.	100	Small.	Scanty.	—
0.24	150	4.5	White, dull.	23.3×10^{-7}
0.20	200	5.0	White, dull.	28.7×10^{-7}
0.23	250	5.0	Grey, metallic.	24.6×10^{-7}
*0.53	750	8.5	Very bright.	10.5×10^{-7}

determined from Laue's equations, as shown below. Table I. refers to the deposits obtained at 30° C., Table II. to those at 50° C., and Table III. to those at 70° C. The results are illustrated by the graphs in fig. 2, and it can be seen at once that there appears to be a definite connexion between

line breadth or grain-size of a deposit and the current density and temperature at which that deposit is obtained. Repetition of the experiments reproduces the same results.

The following points of interest appear:—Firstly, at a given temperature, as the current density is varied there is a minimum on the graph corresponding to a maximum of grain-size. Secondly, at values of the current density less than that for the maximum the curves show that the grain-size decreases rather rapidly with current, the grain-size being taken, as it is shown below, approximately to vary inversely as the line breadth; at values above this critical current density the above variation is less marked, especially when the temperature of the bath is less than 50° C.; it would be easier therefore, by working the bath under

Fig. 2.



the corresponding conditions, to obtain less variation in the deposits by small irregularities of current and temperature. Thirdly, there is a general sort of relation between the grain-size and the nature of the deposit, as shown in the tables. Invariably the highly brilliant deposits go with the smaller, almost amorphous, grain-sizes. This connexion is discussed further below.

Calculation of Grain-size and Effect of Shape.

From Laue's investigation⁽¹⁰⁾ it follows that the half-breadth B of an interference line, obtained by photographing a narrow cylinder of material by the Debye method, is connected with a number η_h , which is a measure of the grain-size of the diffracting material by the following relation⁽⁷⁾:

$$\eta_h = \frac{\omega}{2} \left[\frac{B \cos \theta}{\pi} - \frac{\pi}{B} \left(\frac{r}{R} \right)^2 \cos^3 \theta \right], \quad \omega = \frac{1}{1.8} \dots (1)$$

Here r is the radius of the cylinder forming the specimen, R the radius of the circular camera, and θ the glancing angle for the line on which B is measured. For a cubic lattice, which includes the cases under consideration, the grain-size is related to η_h by

$$\eta = \frac{\lambda}{4\pi} \sqrt{\frac{1}{a^2} \cdot \frac{\sum \left(\frac{h_i}{m_i}\right)^2}{\sum h_i^2}}, \dots \dots (2)$$

where λ is the wave-length of the incident beam, a is the side of the unit-cell, h_i the indices defining the interference line, and m_i the number of times the edge a_i is contained in the whole grain.

If the grains on the average are of the same dimensions in all directions, then equation (2) becomes

$$\eta = \frac{\lambda}{4\pi ma}. \dots \dots (3)$$

From equations (1) and (3), B , θ , R , and r being known, the grain-size can be estimated. This was done for each deposit, and the results are given in the last column of Tables I., II., and III. It is seen that the deposits are remarkably fine-grained. The variation of grain-size with current has already been discussed.

In this connexion it is interesting to record the following curious observations apparently arising from the preferential formation of particular shapes of grains. The effect is illustrated in figs. 3, 4, and 5 (Pl. XVIII.). Here fig. 3 is the photograph of the deposit obtained with a current density of 750 milliamps per sq. cm. at 30°C. It shows a normal distribution of intensity, characteristic of a body-centred cubic specimen, among the spectral lines, the (211), the (200), and the (110) appearing on the photograph, which is taken with chromium rays. It is moreover typical of the dull matt deposits. Fig. 4 (Pl. XVIII.) is the photograph of a specimen obtained at 70°C. with a current density of 250 milliamps. per sq. cm. Here the intensity distribution is not normal. The (200) line is much too weak in comparison with the other two. This photograph is typical of the fairly bright deposits. In fig. 5 (Pl. XVIII.) the (200) line has disappeared altogether. This particular deposit was obtained at 50°C. with a current density of 150 milliamps. per sq. cm., and it gives the typical photograph of the highly brilliant kind of deposit. The explanation of this anomalous distribution of intensities, apparently associated with the brilliance of the deposits, was hardly to be ascribed to

changes in atomic structure, because it is hard to conceive such a marked change in the (200) line without other changes in the spectrum. Also, examination for signs of orientation gave negative results. The metal, moreover, is presumably in a reasonably pure state so far as the presence of other atoms capable of regularly diffracting X-rays is concerned. The presence of such foreign atoms would permit of an explanation in various ways. The probable cause is the development amongst the grains, particularly of those composing the highly lustrous coatings, of a particular feature of shape. In this case equation (3) is not applicable, and equation (2) must be used. The physical interpretation would be that if, owing to the prevalence of, say, a plate-like shape amongst the grains, there is a much less number of certain planes in the grain, then the resolving power of these planes is abnormally diminished and the corresponding spectral line much less visible in comparison with the other sets of planes. The point has been developed mathematically by Brill⁽¹¹⁾, and may be illustrated simply as follows:—

The half-breadth of a line is defined as the ratio of the total intensity of the line to its maximum intensity. A line such as the (200) will be composed of the (200), (020), and (002) contributions. The total intensity, I_0 , reflected by each set, since it depends mainly on the number of diffracting atoms, will be the same. The maximum intensity I_i , depending on the distribution of the atoms in the planes, may differ for the different sets. If b_i be the half-breadth of the component line reflected by one set of planes, then, by definition,

$$b_i = \frac{I_0}{I_i}.$$

The breadth of the composite line, also by definition, is

$$B_0 = \frac{\sum I_0}{\sum I_i} = \frac{n I_0}{\sum \frac{I_0}{b_i}} = \frac{n}{\sum \frac{1}{b_i}}, \quad \dots \quad (4)$$

where n is the number of components.

Electro-deposited body-centred metals tend to deposit themselves with the (111) face set in the plane of the cathode. Although in this case preferential orientation is absent, it might be expected that if the particles develop a particular habit the growth of the (111) plane would be favoured. A trial of this assumption was made. For ease of calculation an orthohexagonal system of axes is chosen in which the corresponding unit vectors will be $a\sqrt{2}$ and $a\sqrt{6}$ in the

cube (111) face; and $a\sqrt{3}$ perpendicular to that face. The appropriate form for η is that for an orthorhombic system of edges m_1a , m_2b , and m_3c , which, by generalizing equation (2), is seen to be

$$\eta = \frac{\lambda}{4\pi} \sqrt{\frac{\left(\frac{h_1}{m_1a}\right)^2 + \left(\frac{h_2}{m_2b}\right)^2 + \left(\frac{h_3}{m_3c}\right)^2}{\left(\frac{h_1}{a}\right)^2 + \left(\frac{h_2}{b}\right)^2 + \left(\frac{h_3}{c}\right)^2}} \quad (5)$$

If we take $m_1=m_2=m$ and $m_3=pm$, then for the orthohexagonal case ⁽¹¹⁾

$$\eta = \frac{\lambda}{4\pi} \sqrt{\frac{\frac{h_1^2}{4} + \frac{h_2^2}{36} + \frac{h_3^2}{9p^2}}{\frac{h_1^2}{2} + \frac{h_2^2}{6} + \frac{h_3^2}{3}}} \cdot \frac{1}{ma} = \frac{\lambda}{4\pi ma} \cdot Z. \quad (6)$$

Now we have in practice from equation (1), since $\left(\frac{r}{R}\right)^2 \cos^3 \theta$ can be made very small,

$$\eta = \frac{\omega}{2} \frac{B \cos \theta}{\pi},$$

so that from (6)

$$b = \frac{\lambda}{2\omega \cos \theta} \cdot \frac{Z}{ma},$$

and from (4), for the composite line,

$$B_0 = \frac{n\lambda}{2\omega \cos \theta ma \Sigma Z} \cdot \cdot \cdot \cdot \cdot \quad (7)$$

Considering now the (200) group, which in the orthohexagonal system become the $\bar{2}22$, 042, and 222, we obtain for B_0

$$B_0 = \frac{K}{\cos \theta ma} \cdot \frac{1}{p \left[4 \sqrt{\frac{1}{10p^2 + 4}} + \sqrt{\frac{1}{p^2 + 1}} \right]},$$

K = constant.

From this it would appear that if p were small B could be greatly broadened, and the line would possess a less and less degree of visibility.

It may also be shown, assuming a rectangular grain in which $a=b=c$, and substituting in (5) for the 200, 002, and 020, that in this case

$$B_0 = \frac{K}{\cos \theta ma} \cdot \frac{1}{p+2}.$$

Now B_0 cannot be increased appreciably by any choice of p , so that only certain shapes of grain would cause the effect. In view of the assumptions already implicit in Laue's equations it is not proposed to attach precise values to p . A grain which tends to grow parallel to the octahedral face would, however, explain the anomalous disappearance of the (200) line.

In the tables those deposits which when photographed gave a spectrum in which the (200) line was absent are marked with an asterisk. Invariably it was found that such deposits were of the highly brilliant variety. The development of this particular habit would appear to be one factor associated with the formation of the high polish. A bright deposit under almost all the plating conditions appears practically at once on immersion. Such a deposit is, of course, too thin to give a diffraction pattern. Further deposition causes it to retain or lose the brilliance, according to the temperature and current conditions. If retained the above feature is exhibited, and if lost the spectrum is normal. One could imagine therefore that the first few layers of atoms are regularly arranged so as to reproduce in the thicker bright deposits this regularity as a flat type of grain. In the matt type the regularity is lost.

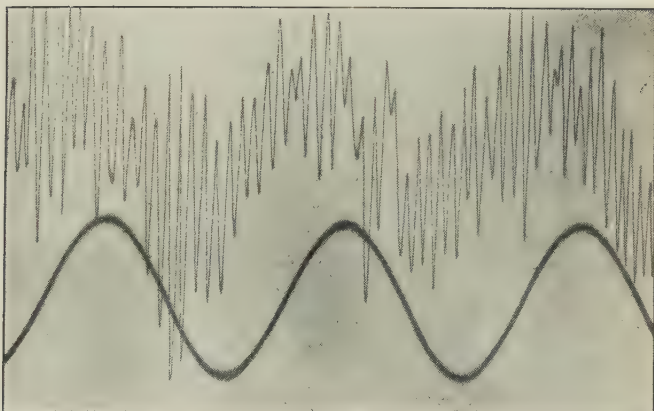
In conclusion, the author desires to express his indebtedness to Mr. J. R. Clarkson, B.Sc., for very great help in obtaining the deposits and making the relevant measurements thereon, and also to Dr. G. W. C. Kaye for his interest and for the provision of facilities necessary to the investigation.

References.

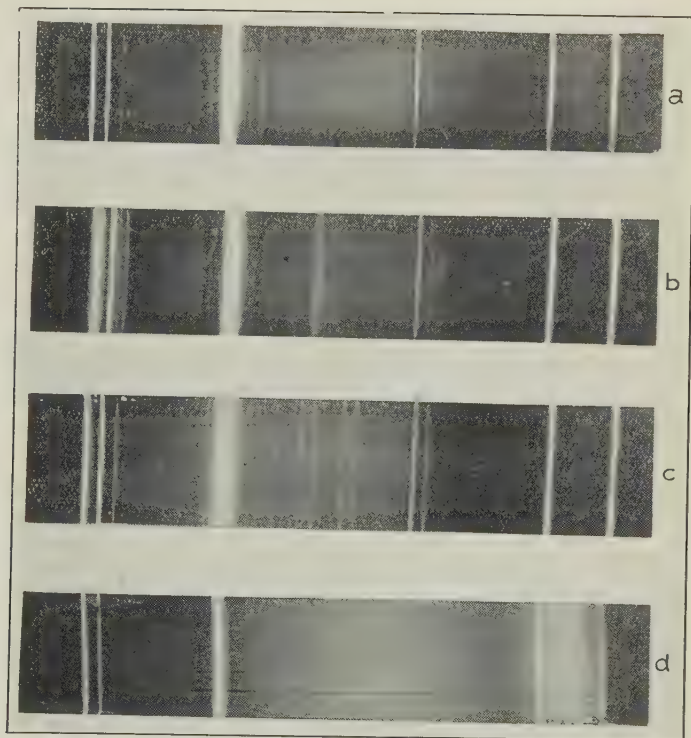
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FIG. 11.



Record of acoustic output from the diaphragm of fig. 10 and Table V. when driven at its first radial mode, namely, 49·2 cycles per second by a steady current in the (coil heavy sine wave). Impulsing due to asymmetry of motion causes oscillations of the same frequency as the second centre moving symmetrical mode to be superposed on the 49·2 cycle radiation.

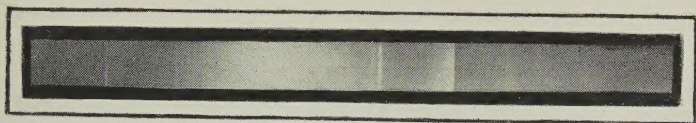


- (a) Dichloroacetic acid.
- (b) Amyl nitrate (iso).
- (c) Benzoyl Chloride (with filter).
- (d) Benzoyl Chloride (without filter)

— 3243 Å

— 3591 Å

— 3881 Å

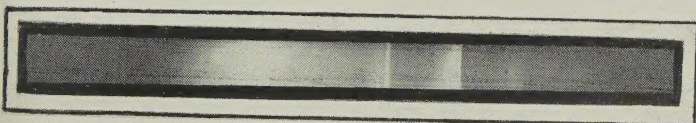


Room
temperature

— 3212 Å

—

—

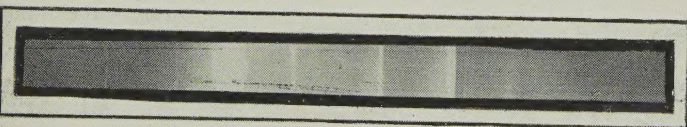


Liquid
air

— 3200 Å

—

—

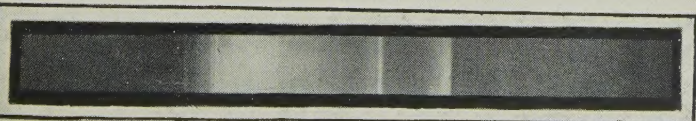


Liquid
hydrogen

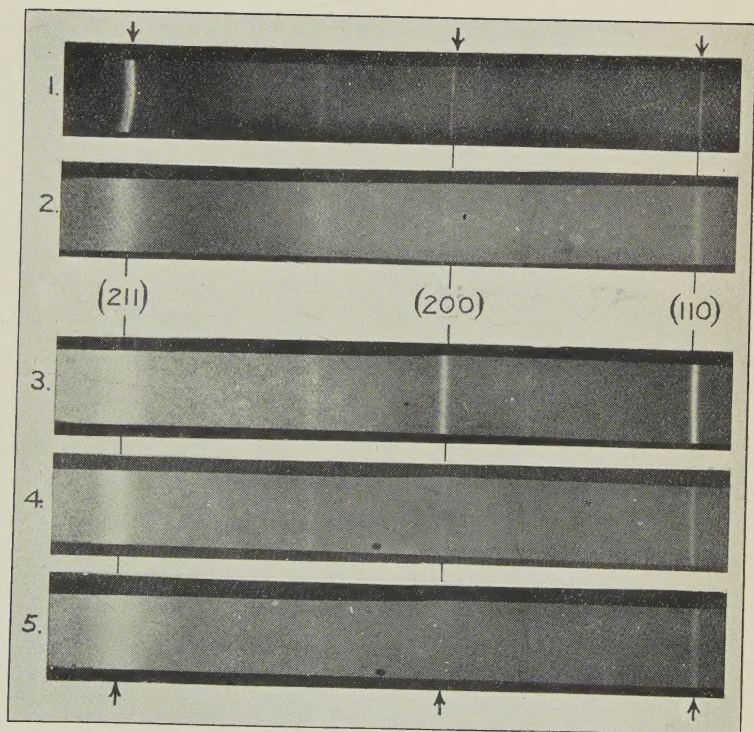
— 3198 Å

—

—



Liquid
helium



X-ray Examination of Electroplated Chromium Coatings.

